THE

PHYSICAL SOCIETY

OF

LONDON.

PROCEEDINGS.

VOLUME XXI.—PART II.

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1908.

PHYSICAL SOCIETY OF LONDON.

1907–8.

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Royal College of Science.

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PROCEEDINGS

AT THE

MEETINGS OF THE PHYSICAL SOCIETY

OF LONDON.

SESSION 1907–1908.

February 8th, 1907.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

The following Candidates were elected Fellows of the Society:—
L. Bairstow, J. de G. Hunter, C. Jakeman, C. H. Lees, C. C. Paterson, E. H. Rayner, W. Rosenhain, and F. E. Smith.

The following Paper was read:—
The Magnetic Fields and Inductive Coefficients of Circular, Cylindrical, and Helical Currents. By Mr A. Russell.

February 22nd, 1907.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

The following Candidates were elected Fellows of the Society:—
W. H. Bragg and C. A. B. Garrett.

Prof. Perry announced that the Council had elected Dr W. H.

Eccles as a Member of Council to fill the vacancy caused by the resignation of Prof. H. A. Wilson, F.R.S.

The following Papers were read:—

1. Transformer Indicator Diagrams. By Prof. T. R. Lyle.

2. The Ionization of Gases by α Particles of Radium. By Prof. W. H. Bragg.

March 8th, 1907.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

The following Candidates were elected Fellows of the Society:—
E. Boardman, G. H. Martyn, and J. S. G. Thomas.

The following Paper was read:—

The Rate of Recovery of Residual Charge in Electric Condensers. By Prof. F. T. Trouton, F.R.S., and Mr S. Russ.

March 22nd, 1907.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

The following Candidates were elected Fellows of the Society:—
W. D. Butcher, E. Rutherford, and W. Thomson.

The following Papers were read:—

1. Experimental Mathematics. By Mr Pochin.

2. Logarithmic Lazytongs and Lattice-work. By Mr Blakesley.

Mr R. J. B. Roberts exhibited a Compensating Micro-manometer.

April 26th, 1907.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

The following Candidates were elected Fellows of the Society:—
T. Ayres, A. Blackie, Jun., F. L. Hopwood, S. Russ, and W. A. Scoble.

The following Papers were read:—

1. Electrical Conduction produced by Heating Salts. By Mr A. E. Garrett.

2. The Influence of Pressure upon Convection Currents. By Mr W. S. Tucker.

Mr W. B. Croft exhibited some Solenoids which are turned by the Earth's Magnetic Field, and some other Electrical Apparatus.

Mr J. A. Tomkins exhibited a Simple Apparatus for mechanically illustrating the tangent and the sine laws.

May 10th, 1907.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

The following Paper was read:—
Stereoscopy with long Base-line. By Dr T. C. Porter.
The effects were illustrated by examples on the screen.

May 24th, 1907.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

The following Candidates were elected Fellows of the Society:—
Mrs Hertha Ayrton and A. E. Hodgson.

The following Papers were read:—

1. The Measurement of Mutual Inductance by the aid of a Vibration Galvanometer. By Mr A. Campbell.

2. The Rate of Decay of the Active Deposit from Radium. By Messrs. W. Wilson and W. Makower.

Mr S. G. Brown exhibited an apparatus for Relay Working of long Submarine Telegraph Cables.

June 14th, 1907.

Meeting held at University College.

Mr H. M. Elder, Vice-President, in the Chair.

The following Paper was read:—

Observations on the Electric Arc. By Mr W. L. Upson.

Dr J. A. Fleming showed experiments upon the Poulsen Arc as a means of producing electrical oscillations.

Mr R. Appleyard exhibited a Direct-Reading Conductivity-Bridge for rods.

June 28th, 1907.

Meeting held at the Central Technical College.

Prof. W. E. Ayrton, F.R.S., Past-President, in the Chair.

The following Candidate was elected a Fellow of the Society:—

O. V. Thomas.

The following Papers were read:—

1. A Cosine Flicker Photometer. By Mr J. S. Dow.

2. Some Phenomena in Colour Vision. By Mr J. S. Dow.

3. The Production of Sand-Ripples on the Sea-shore. By Mrs Ayrton.

Mr J. T. Irwin gave a demonstration of his Hot Wire Oscillographs and Wattmeters.

October 25th, 1907.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

The following Papers were read:—

1. The Use of Variable Mutual Inductances. By Mr A. Campbell.

2. Magnetic Oscillators as Radiators in Wireless Telegraphy. By Dr J. A. Fleming, F.R.S.

November 8th, 1907.

Meeting held at the Royal College of Science.

Dr C. Chree, F.R.S., Vice-President, in the Chair.

The following Candidate was elected a Fellow of the Society :—
J. M. Gordon.

The following Papers were read :—

1. A Graphic Method for Stream Lines and Equipotential Surfaces. By Mr L. F. Richardson.

2. The Lateral Vibration of Bars supported at two points with one end overhanging. By Dr J. Morrow.

November 22nd, 1907.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

Mr Skinner exhibited specimens of Singing Sand.

Mr L. Bairstow exhibited a Micromanometer.

Prof. C. V. Boys, F.R.S., showed a Diabolo Experiment.

Prof. H. A. Wilson, F.R.S., exhibited a Gyroscope illustrating Brennan's Mono-railway.

December 13th, 1907.

Meeting (informal) held at the Royal College of Science.

An Exhibition of Apparatus was given by the following firms :— Messrs. R. & J. Beck, Ltd.; The Cambridge Scientific Instrument Co., Ltd.; Casella & Co.; Crompton & Co.; Elliott Bros.; Everett, Edgcumbe & Co.; Evershed & Vignoles; Clark Fisher & Wadsworth; Gambrell Bros.; J. J. Griffin & Sons; A. Gallenkamp & Co.; A. Hilger Ltd.; Leslie Miller; Nalder Bros. & Co.; Nalder Bros. & Thompson; Newton & Co.; R. W. Paul; James Pitkin & Co.; Ross Ltd. There was also an Exhibit by the Meteorological Office.

January 24th, 1908.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

The following Candidates were elected Fellows of the Society :—
J. G. Howarth and R. S. Smith.

The following Paper was read :—
Recalescence Curves. By Mr W. Rosenhain.

Annual General Meeting.

February 14th, 1908.

Meeting held at the Royal College of Science.

Prof. J. Perry, F.R.S., President, in the Chair.

The following Report of the Council was read by the Secretary :—

Since the last Annual General Meeting, thirteen ordinary Science Meetings and one informal Meeting of the Society have been held. Of these, twelve were held at the Royal College of Science; one, that on June 14th, was held at University College, by invitation of Prof. J. A. Fleming, F.R.S., and one, that on June 28th, at the Central Technical College, by invitation of Prof. W. E. Ayrton, F.R.S. The average attendance at the Meetings has been 58 as compared with 50 during the preceding year.

The third Annual Exhibition of Apparatus by Manufacturers was held on December 13th, when the attendance of Fellows and Visitors amounted to about 200.

Light refreshments are now provided before the Afternoon Meetings and after the Evening Meetings. This innovation appears to be appreciated, and it is hoped that the opportunity thus afforded will enable Fellows to become personally acquainted with each other, and to interchange opinions more readily than has been possible hitherto.

The number of ordinary Fellows now on the roll, as distinct from Honorary Fellows, is 437, an increase of 11 on the number last year; 27 new Fellows have been elected, two Fellows have been reinstated, and two Honorary Fellows, namely, Prof. Gabriel Lippmann and Prof. Simon Newcomb, have been elected. There have been 11 resignations, the names of two Fellows have been

struck off the List for non-payment of subscriptions; and the Society has to mourn the loss by death of 6 Fellows, namely, one Honorary Fellow, P. J. C. Jules Janssen, and 5 ordinary Fellows, namely, Lord Kelvin, Sir W. Perkin, J. R. Brittle, J. MacFarlane Gray, and J. W. Kearton.

The Report of the Council was adopted.

The Report of the Treasurer and the Balance Sheet were presented and adopted.

The election of Officers and other Members of Council then took place, the new Council being constituted as follows :—

President.—C. Chree, Sc.D., LL.D., F.R.S.

Vice-Presidents who have filled the Office of President.—Prof. G. C. Foster, F.R.S.; Prof. W. G. Adams, M.A., F.R.S.; Prof. R. B. Clifton, M.A., F.R.S.; Prof. A. W. Reinold, M.A., F.R.S.; Prof. W. E. Ayrton, F.R.S.; Prin. Sir Arthur W. Rücker, M.A., D.Sc., F.R.S.; Sir W. de W. Abney, R.E., K.C.B., D.C.L., F.R.S.; Shelford Bidwell, M.A., LL.B., F.R.S.; Prin. Sir Oliver J. Lodge, D.Sc., F.R.S.; Prof. S. P. Thompson, D.Sc., F.R.S.; R. T. Glazebrook, D.Sc., F.R.S.; Prof. J. H. Poynting, M.A., D.Sc., F.R.S.; Prof. J. Perry, F.R.S.

Vice-Presidents.—W. Duddell, F.R.S.; H. M. Elder, M.A.; Prof. J. A. Ewing, F.R.S.; W. Watson, D.Sc., F.R.S.

Secretaries.—W. R. Cooper, M.A.; Prof. W. Cassie, M.A.

Foreign Secretary.—Prof. S. P. Thompson, D.Sc., F.R.S.

Treasurer.—Prof. H. L. Callendar, M.A., LL.D., F.R.S.

Librarian.—W. Watson, D.Sc., F.R.S.

Other Members of Council.—A. Campbell, B.A.; W. H. Eccles, D.Sc.; A. Griffiths, D.Sc.; J. A. Harker, D.Sc.; Prof. C. H. Lees, D.Sc., F.R.S.; T. Mather, F.R.S.; A. Russell, M.A.; S. Skinner, M.A.; S. W. J. Smith, M.A.; Prof. L. R. Wilberforce, M.A.

Votes of thanks were passed to the Auditors, to the Officers and Council, and to the Board of Education.

Prof. J. Perry, F.R.S., the retiring President, then vacated the Chair in favour of Dr C. Chree, F.R.S., who delivered his Presidential Address.

Treasurer's Report.

The position of the Society this year shows a decided improvement. There are more new members than usual, and subscriptions have been paid more punctually. The balance in bank has increased by nearly £240, more than £100 of which, however, is due to composition-fees and recovered income-tax. The value of the securities has declined somewhat owing to the general depression, but this is probably of a temporary nature. There are no outstanding liabilities, and the income shows a healthy tendency to exceed the expenditure.

HUGH L. CALLENDAR,
Hon. Treasurer.

The Treasurer in Account with the Physical Society, from January 1st, 1907, to December 31st, 1907.

Dr.	£	*s.*	*d.*	£	*s.*	*d.*
Jan. 1, 1907. Balance in Bank				176	7	7
Entrance-Fees	28	7	0			
Subscriptions	443	3	5			
Extra Subscriptions	29	6	0			
Arrears	54	12	0			
Abstracts etc.	8	7	6			
				563	15	11
Composition-Fees				84	0	0
Dividends:—						
Furness Debenture Stock	15	3	10			
Metropolitan Board of Works	6	13	0			
Lancaster Corporation Stock	11	8	0			
New South Wales	8	9	0			
Midland Railway	38	0	0			
Great Eastern Railway	19	0	0			
London, Brighton, & South Coast Railway	24	18	10			
				123	12	8
Sales of Publications				37	15	8
Income Tax recovered (3 years)				19	8	6
				£1005	0	4

Cr.	£	*s.*	*d.*	£	*s.*	*d.*
Science Abstracts				279	6	0
Taylor and Francis:—						
Proceedings	113	12	9			
Abstracts, etc.	83	19	0			
Distribution	14	14	6			
Separate Copies	16	13	0			
				228	19	3
Periodicals				3	9	0
Binding				7	9	8
Reporting				35	0	0
Royal Asiatic Society				2	2	0
Attendance				7	10	0
Petty Cash (Treasurer and Secretaries)				11	13	6
Refreshments				8	14	6
Commissions and Postages				9	0	
Apparatus				2	12	0
R. S. Subscription and Cheque unpaid				2	2	0
Balance in Bank				415	13	5
				£1005	0	4

Audited and found correct,

HUGH L. CALLENDAR, *Honorary Treasurer.*

20th January, 1908.

CHARLES SELBY WHITEHEAD,
HENRY R. J. BURSTALL, } *Auditors.*

PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY, DECEMBER 31, 1907.

ASSETS.

	£	s.	d.
Subscriptions due, Treasurer's estimate	50	0	0
£533 Furness Ry. Co. 3 per cent. Debenture Stock	421	0	0
£1600 Midland Railway 2½ per cent. Preference Stock	1088	0	0
£200 Metropolitan Board of Works 3½ per cent. Consolidated Stock	202	0	0
£400 Lancaster Corporation 3 per cent. Redeemable Stock	332	0	0
£284 2s. 9d. New South Wales 3½ per cent. Inscribed Stock	249	0	0
£500 London, Brighton, and South Coast Railway Ordinary Stock	510	0	0
£500 Great Eastern Railway 4 per cent. Debenture Stock	550	0	0
Balance in Bank	415	13	5
Publications in Stock, estimated	200	0	0
	£4017	13	5

LIABILITIES.

	£	s.	d.
Balance	4017	13	5
	£4017	13	5

HUGH L. CALLENDAR, *Honorary Treasurer.*

20th January, 1908.

Audited and found correct,

CHARLES SELBY WHITEHEAD,
HENRY R. J. BURSTALL, } *Auditors.*

Presidential Address to The Physical Society of London,

14th February, 1908.

C. CHREE, Sc.D., LL.D., F.R.S.

The losses of the Society by death since the last general meeting have been few, but they include two most distinguished Fellows, Lord Kelvin and Sir W. H. Perkin. Both joined the Society in 1875, Perkin in January, Kelvin in June. The work with which Perkin's name is generally associated was chemical, and does not call for prolonged comment here. It must have been a great satisfaction to all who knew him, that he lived long enough to receive the remarkable international tribute which but shortly preceded his death. Lord Kelvin was one of our earliest presidents. During his lifetime British Physicists had the satisfaction of feeling assured that amongst their number was one who was universally recognised as the foremost man in his department of knowledge. There have already appeared several obituary notices of Lord Kelvin by old pupils and others having much more intimate knowledge of him personally than I possess. Especially would I refer to an article by Prof. Ayrton in the 'Times,' possessing that touch of the imagination which is essential to a life-like portrait. Lord Kelvin was active in a great variety of fields, appealing to very varied types of mind, and to different classes of the community. The fact that he, an eminent pure scientist, was the inventor of electrical and nautical instruments of the highest practical utility, has been, I think, a most potent cause in impressing the value of science on the average English mind—I say English advisedly. It is one of the chief reasons why English physicists are recognised by their countrymen and countrywomen as having some claim to be regarded as useful units in the population. Another side of Lord Kelvin's activity also appealed strongly to the public imagination. I refer to his fondness for formulating theories as to matters of general interest, such as the internal state or age of the earth, or the supply of solar heat. These I regard rather in the light of scientific poetry. It is considered the privilege of the young to dream dreams, and Lord Kelvin's mind was always young. Without imagination we

should lose most of the pleasures of life, and the imaginings of a mind like Lord Kelvin's, even in subjects where facts are still sadly deficient, are likely to possess interest for all future workers in the field. But apart from what appeals to the popular mind, Lord Kelvin's writings contain a vast amount of solid and most original work. He made substantial contributions to Hydrodynamics and Thermodynamics, to Heat, Electricity, Magnetism, Elasticity, and Optical Theory. Of the subjects he has dealt with, Elasticity is the one on which I am most qualified to speak. The prominent feature in his work in that department is the tendency to give theory a form leading to concrete practical applications. When it was absolutely necessary, Lord Kelvin carried out intricate mathematical calculations of considerable length; but whilst he was undoubtedly an able analyst, analysis seemed with him always a means to an end. Once the end was reached, the perfection of the analysis, or its extension so as to reach results of greater symmetry or more generality, did not seem to appeal to him. Not infrequently, indeed, he did not take the trouble to publish the analysis at the time. The reason was certainly not mental inertia, quite the contrary. It was due, I think, to his intense mental activity. He had a constant flow of new ideas, one treading on the heels of another; and before any one idea had received a long exposure on the stage of his mind, another was pressing to take its place. Lord Kelvin almost at once obtained the recognition which his powers merited. He was not exposed when young to a lack of appreciation such as sometimes serves to sour those to whom distinction comes late in life. But allowing for all this, the generosity with which he recognised the value of the work of younger and unknown men was a very pleasing feature of his character.

Turning to the question of the progress of the Society, I learn from Mr. Cooper that since 1903 our membership has increased by 30, or fully 7 per cent. With the increased number of persons concerned directly or indirectly with Science, one would naturally expect an increase in the membership of Societies such as ours; but this tendency is opposed by increased specialisation and the consequent rise of new Societies. Considering modern tendencies, one class of the community from which I think we might reasonably have expected substantial support has accorded it but slightly. Ladies are freely admitted to our membership, but for some reason they have not hitherto shown much eagerness to

avail themselves of this opportunity. As an additional encouragement to them, I might refer to a recent departure, viz., the supply of tea and other light refreshments at the meetings. Tea at the Royal Society affords an opportunity for many valuable conversations, and I see no reason why tea at the Physical Society should not prove similarly useful. This departure is due, I think, in considerable measure to the more optimistic attitude which our Treasurer finds himself able to take with regard to our financial position.

Another domestic occurrence I wish to refer to is a resolution of the Council intended to encourage speakers, especially the authors of papers, to be reasonable in the demands which they make upon the bank of time. The resolution runs: "That with the object of facilitating discussion, the reader of a paper already printed and distributed should be invited to limit himself to 20 minutes or to such time as the Chairman may think desirable, and speakers on the discussion to 10 minutes."

When there are several papers of some length down for reading, it is obviously impossible for all the authors to go into minute details unless the duration of the meeting is unduly prolonged. Papers of importance are usually in type and proofs are obtainable before the meeting. Those who are specially interested in the subject would most naturally derive *details* from the proof. The course most likely to be generally useful is for the author, after a brief *resumé* of previous knowledge, to give an outline of the leading new principles or results which he has reached, in a form intelligible to those who are not specialists. Such a statement, especially when accompanied by a few experiments or lantern-slides, will supply the average hearer with all he is likely to assimilate. The discussion after the paper is read should afford specialists the opportunity of criticising or of seeking explanations on specific points. It is obvious that if many Fellows wished to speak for 10 minutes, the time available for discussion would soon be exhausted. But all that most speakers have to say on a paper can usually be said in 5 minutes or less. It will be my object when in the chair to give effect to the spirit of the resolution; but its success must depend largely on the reasonableness of individuals, and I trust that Fellows will not be found lacking in this possession. Before leaving the subject, I would express a hope that more of our ex-presidents may find it possible to put in an occasional appearance. Their intervention in discussions would,

I am sure, be generally appreciated, and prove an encouragement to those contributing papers.

I propose now to give a brief *resumé* of the results of some work which has occupied a good deal of my attention during the last two or three years. The National Antarctic Expedition of 1901–4 was supplied with magnetographs, and the reduction and discussion of the curves was entrusted to the National Physical Laboratory. The work is still in progress, and when finally completed the results will appear in the official volumes of the Expedition. It occurred to me, however, that a preliminary account of some of the outstanding phenomena, on an occasion such as this, might serve a useful purpose; and this view, I am glad to say, recommended itself to the authorities of the Royal Society and the Director of the National Physical Laboratory.

When referring to any British national undertaking, such as a war or a scientific expedition, one is expected to apologise for a greater or less amount of preliminary muddle. Perhaps as a variant I may be allowed to say a few words as to what should in my opinion be done when the next National Scientific Expedition is being prepared. Supposing the physical programme as extensive as in the late expedition, comprising subjects so large and diverse as Terrestrial Magnetism, Atmospheric Electricity, Auroral observations and determinations of Gravity, there ought to be at least two physical observers. These ought to be men of first-class University attainments, having a thorough knowledge of general physics, assuming that such men can be got who are at the same time strong, hardy, and persevering. Before the expedition sets out they should devote at least 6 months—better 12—to a special study of the subjects they will have to deal with, so as to obtain at least a general knowledge of the leading phenomena on which it is hoped that the expedition will throw further light. They should also make themselves thoroughly competent as observers. All the apparatus for the expedition should be ready and thoroughly tested at least three months before the expedition sets out, and the observers should use this apparatus sufficiently to become entirely at home with it. A programme should be drawn up, and the observers practised in its execution. To give confidence to the public, and represent different interests, it is probably necessary on such an occasion that committees of a somewhat unwieldy size should be nominated; but these committees should delegate the construction of the programme for each

subject to one or two men who have an intimate knowledge of its recent developments, the general body contenting itself with seeing that the programme is based on common-sense as well as on special technical knowledge. The programme should be drawn up in ample time to admit of the observers being practised in its execution. Such a programme is not to be regarded as a cast-iron statute, because no one can foresee exactly what is going to happen; but it ought to make absolutely clear what are the physical aims of the expedition, and what are the most likely means of attaining them. The necessity for a programme would no doubt be lessened if the expedition were under the command of a Physicist of resource and ripe experience. But if—as is most likely—it is under the command of some one whose knowledge of physical science is very limited, it is eminently desirable that some authoritative instructions should exist which will ensure that opportunities for promoting the scientific objects of the expedition shall be utilised to the utmost. It might also serve a useful purpose—though in so hurried an era as ours the idea may appear quixotic—if, on the return of the expedition and after a general examination of its results, something equivalent to a scientific court-martial were held by a competent judicial body whose expressions of approval or blame would carry weight. As matters stand, the observer who confines himself to purely scientific work—however efficient—can have no assurance that he will not be entirely overshadowed by the doers of exploits which appeal to the popular imagination.

Returning now to the 'Discovery' 1901–4 Expedition: at the start the fates were most unpropitious. First one and then a second physicist was laid aside, and within a very short time of the date when the Expedition was due to sail there was no physical observer; whilst the magnetographs, which had been ordered in Germany, had not yet reached this country. Fortune then began to change. The Expedition secured the services of Mr. Bernacchi, who had but recently returned from the 'Southern Cross' Expedition, which was the first to spend a winter in the Antarctic. The 'Discovery' sailed, leaving Mr. Bernacchi to follow with the pendulum apparatus and the magnetographs, after obtaining such practice as time might allow. The magnetographs then turned up at Kew, though not until I had left on my annual holiday. They proved to be of a type absolutely strange to all at Kew, and requiring more delicate

handling than the ordinary Kew pattern. Fortunately the services of Dr. Harker and Mr. F. E. Smith were available, and they succeeded in erecting the instruments and getting them to work. Mr. Bernacchi, however, had only a few days' experience of them before he had to set sail. On returning from my holiday, I was somewhat perturbed to be met with high encomiums of the magnetographs on the ground of their sensitiveness. They had shown the wickedness of the electric trams, then a burning topic, in a particularly effective manner. I should have been still more perturbed if I had known that the quartz-fibre which carried the horizontal-force magnet when at Kew was the stoutest of the large number supplied. Such, however, proved to be the case, and as that fibre was broken ere the Antarctic was reached, it fell to Mr. Bernacchi to replace it by a succession of fibres giving the instrument a sensitiveness four or five times that customary in Europe. The natural result was a not infrequent loss of trace, and a lot of extra trouble to the observer and to those who have had to reduce the curves. The sensitiveness of the declination magnetograph—regarded as a measurer of angles—was little over half that of the Kew magnetograph ; but in the Antarctic, where the horizontal force was only about a third of that in England, it had as a measurer of force a sensitiveness some 50 per cent. greater than that of the Kew magnetograph at Kew. If the sensitiveness of these two instruments had been a fifth of what it actually was, it would have been a great improvement. The third instrument—recording vertical force—as used in the Antarctic did not err in the direction of over-sensitiveness—rather the opposite, but it had unfortunately a very large temperature coefficient. This coefficient can be determined satisfactorily only under the conditions of actual use. To have determined the coefficient at Kew, where the vertical force is opposite in sign to that in the Antarctic, and only three-fifths as large, would have been futile. In the Antarctic, unfortunately, a direct determination was not found feasible, and not the easiest of my labours during the past year has been to extract the necessary information from the Antarctic curves themselves. Thanks to the excellent behaviour of a sensitive self-recording metallic thermometer inside the vertical-force magnet box, and to the nature of the temperature changes experienced, the problem has I think been successfully dealt with ; but the labour of reducing the vertical-force records has been at least trebled. It will, I hope, be clearly

understood that the previous remarks have no bearing on the question of the suitability of the type of magnetograph for use under normal conditions. They are directed solely to explaining wherein the exceptional conditions of the Antarctic had not been provided for. Without some explanation of this kind, it would have been impossible for you adequately to realise the difficulties with which Mr. Bernacchi had to contend, difficulties for which he was in no way responsible, and which no one I think could have encountered with unvarying success. I would take this opportunity of acknowledging the valuable assistance given by Mr. Bernacchi throughout the whole reduction of the magnetic curves. At the start he spent some months at Kew arranging the material, and he tabulated a large proportion of the declination curves. Subsequently the tabulations were carried on by two junior assistants, Mr. Maudling and Mr. Gendle, who both proved most expert and discriminating tabulators, and did excellent work.

I shall now show some lantern-slides, for which I am indebted to Mr. Hugo, of the National Physical Laboratory, which will I hope give a general idea of the principal results derived from the magnetic curves. As a preliminary, I shall show a slide of Kew declination curves (fig. 1), as being of a type more suited to explain the general character of magnetic records. To economise photographic paper, two successive days' records are taken on the same sheet. There are thus two curved lines, each with its corresponding straight base line. The upper curved and the upper base line refer to the first day. The paper is wound round a drum turned by clockwork. The base line is produced by light reflected from a fixed mirror, the pencil of light being interrupted for a few minutes at two-hour intervals, so as to mark the time. The curved line arises from light reflected from a mirror carried by a freely suspended horizontal magnet. The magnet alters its direction as the declination alters, the mirror turning with it, and the reflected light moves across the paper, thus altering the ordinate of the curved line, *i. e.*, its distance from the base line.

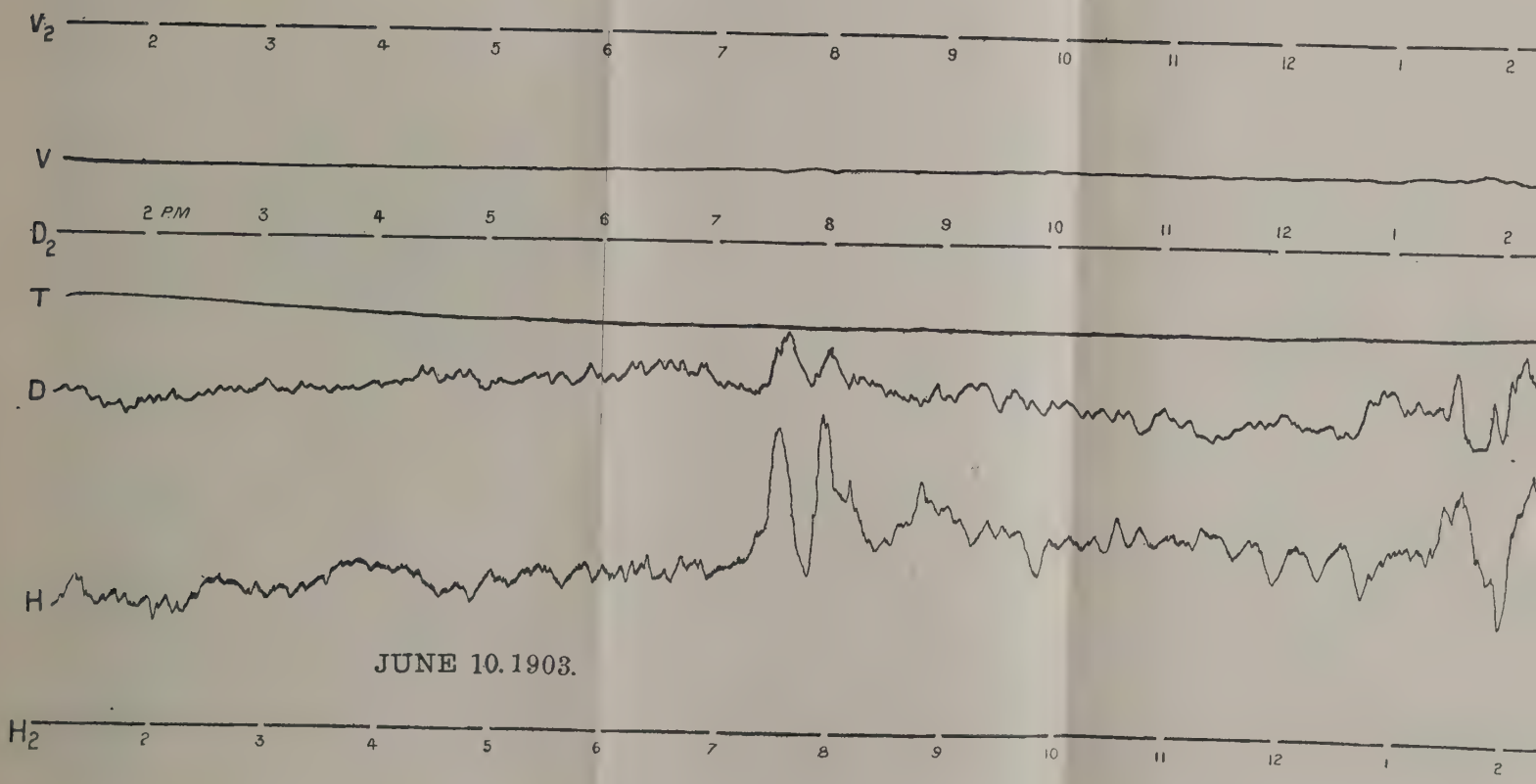
In this case, the positive direction answers to increasing westerly declination, a change of 1 cm. in ordinate meaning a change of 8′·6 in declination*. The equivalent of 1 cm. depends on the distance between the photographic paper and the magnet. If the

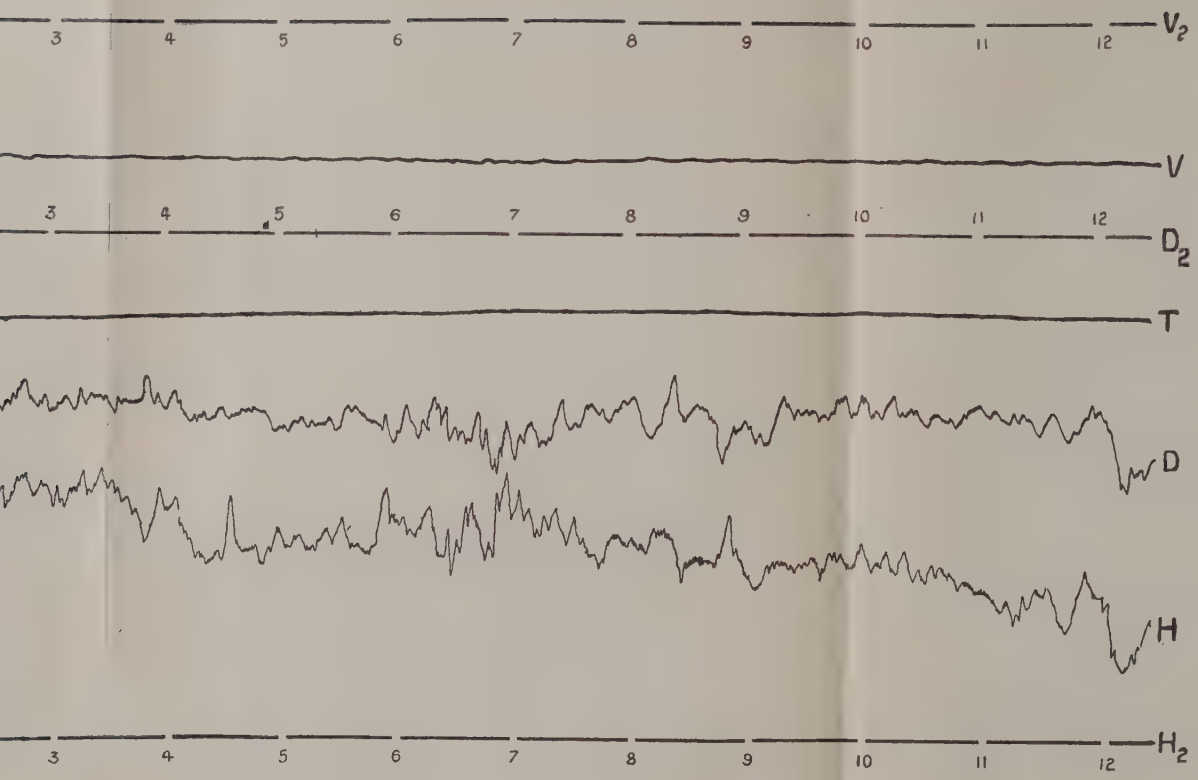
* The curve is reproduced here on a reduced scale, 1 cm. representing approximately 18′ of declination.

Fig. 1.—KEW DECLINATION, 1895 { September 6 10 13 to 7 10 13 A.M. G.M.T.
" 7 10 15 " 8 10 8 " "

[*To face* p. xix.

FIG. 2.—ANTARCTIC CURVE




V2
3
4
5
6
7
8
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10
11
12
V
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10
11
12
D2
T
D
H
H2
3
4
5
6
7
8
9
10
11
12

instrument remains untouched, the base line should answer to a certain constant declination, whose value is determined by reference to the absolute observations made with a unifilar magnetometer. Suppose, for instance, that the absolute declination observed at a certain time is 16° 30′ W., and that the curve ordinate at this hour is +5 cm. Then the base-line value is less than the observed value by the equivalent of 5 cm., or 43′, and so is 15° 47′ W. From this known value of the base line, and the known equivalent of 1 cm. of ordinate, we can now derive the declination at any specified instant. Fig. 1 represents very quiet magnetic conditions. The large regular increase of ordinate at the start answers to the swing of the magnet to the west in the forenoon and early afternoon, which is the most conspicuous feature of the diurnal variation in England at all seasons of the year.

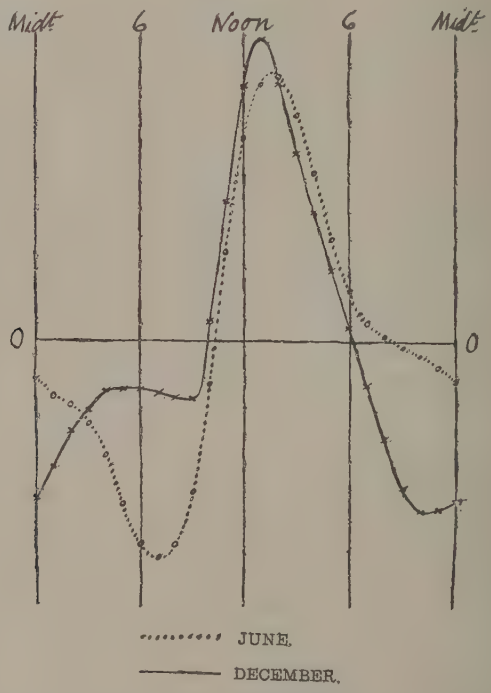
The next slide (fig. 2) represents magnetic curves actually taken in the Antarctic. They present many conspicuous differences from the Kew curves. In the Eschenhagen instrument all three elements—declination, horizontal force, and vertical force—are recorded on one drum. On the other hand, only one day's curves are recorded on each sheet. The curve for each element has its own base line, and in each the trace is interrupted once an hour. In the figure, D, H, and V indicate the Declination, Horizontal Force, and Vertical Force curves respectively, D_2, H_2, and V_2 the corresponding base lines. T indicates the temperature of the metallic thermometer inside the vertical-force magnet-box. It has the same base line V_2 as the vertical-force curve. The day selected, strange as it may appear, represents an unusually quiet state of matters for the Antarctic. The declination and horizontal-force magnets were practically never at rest, and the incessant disturbances render it difficult to recognise the character of the regular diurnal variation. It will be noticed that the D and H curves nearly interfere, and at first one may feel disposed to reflect on the observer for having the traces so near each other. Keeping the traces separate was, however, only one of the objects he had to aim at; a still more important thing was to keep all on the sheet. It was thus prudent to have the traces near the centre of the sheet during quiet times.

The next slide (not reproduced) shows a day of by no means exceptional disturbance. The full width of the sheet answered to nearly 5 of declination, but the declination trace on this occasion

actually crossed from side to side in about 20 minutes. A curious interrelation is visible between the vertical-force and temperature traces, the one coming down the sheet when the other went up. This really arose from the large temperature coefficient of the vertical-force magnet.

When driven at the normal speed, the drum carrying the photographic paper rotated completely in 25 hours. If the observer

Fig. 3.



allowed a longer interval than this to elapse between starting and stopping, a second day's trace began to superpose itself on the first. A margin of one hour in the day proved somewhat narrow for the exigencies of the Antarctic. In particular there were occasional wind storms of such violence that it was too dangerous to venture as far as the magnetic hut, and the observer had to wait until the worst of the storm was over. Exactly the same

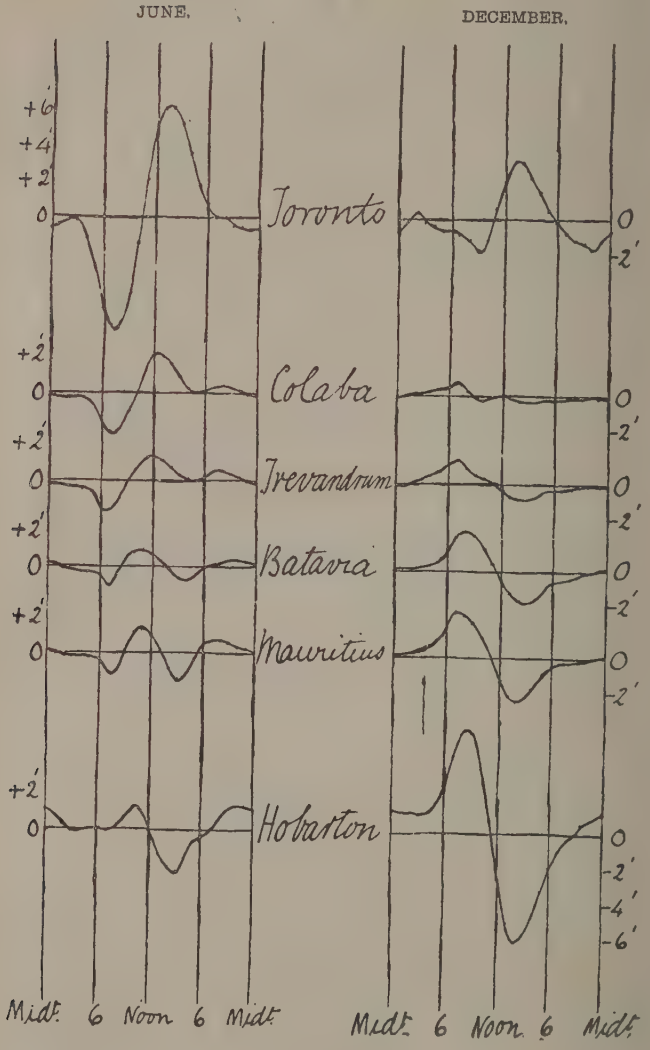
trouble, it may be mentioned, was experienced by the recent American (Ziegler) Polar Expedition in Franz Josef Land. On the rare occasions when a blizzard delayed Mr. Bernacchi's visit to the magnetograph, there was considerable superposition of the traces, and their disentanglement has not always been found possible.

I pass now to the data for the diurnal variation of the magnetic elements, as derived from the curves. To deduce the regular diurnal inequality for a given month or season, one measures the curve ordinate at every hour, finds the mean value for each hour of the 24, and finds the difference between this and the corresponding mean for the entire day. It will again be convenient to illustrate this first by reference to Kew results. Fig. 3 shows the nature of the diurnal inequality of declination at Kew, at midsummer (June) and midwinter (December). The horizontal line OO answers to the mean value for the day. The positive direction in the ordinate signifies that the north end of the magnet is pointing to the west of its mean position. The curves are really drawn to different scales, so chosen as to give the same mean length of ordinate for each. If drawn to the same scale, the June curve would have a range nearly $2\frac{1}{2}$ times that of the December curve.

It will be seen that the curves, though differing slightly in the time of the westerly maximum, still closely resemble one another during those hours of the day when the changes of declination are most rapid, but they differ notably in the early morning.

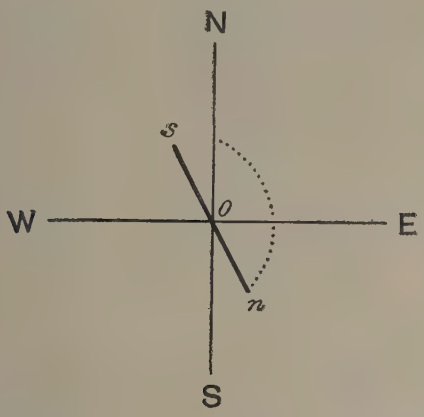
The next slide (fig. 4) is intended to assist in trasferring the imagination to the Southern hemisphere. The curves all show declination, and in all a positive ordinate represents movement of the north pole towards the west. The stations are selected so that pairs possess nearly equal north and south latitudes. Thus Toronto and Hobarton have latitudes about 43°, Colaba and Mauritius about 20°, Trevandrum and Batavia about 7°. As regards climate, the difference between December and June is more marked in high than in low latitudes, but this is not the case as regards the *type* of the declination curve. Looking at either the June or the December curves, one can see a gradual transition from Toronto to Hobarton. Certain inconspicuous features of the midwinter curve in one hemisphere are cases apparently of arrested development, answering to prominent midsummer features in the other hemisphere. But the principal point calling for attention is the nature of the difference between

Fig. 4.


JUNE.
DECEMBER.
+6'
+4'
+2'
0
Toronto
0
-2'
+2'
0
Colaba
0
-2'
+2'
0
Trevandrum
0
-2'
+2'
0
Batavia
0
-2'
+2'
0
Mauritius
0
-2'
+2'
0
Hobarton
0
-2'
-4'
-6'
Midt. 6 Noon 6 Midt.
Midt. 6 Noon 6 Midt.

the June curve at Toronto and the December curve at Hobarton; *i. e.*, the midsummer curves at the extreme stations. They are almost the exact opposites of one another. When the needle at Toronto moves to the west, that at Hobarton moves to the east. In other words, if we drew these two curves so that up the sheet meant movement to the west at Toronto, but movement to the east at Hobarton, they would closely resemble one another. It might thus be expected that in dealing with declination in the Antarctic, the positive direction of the ordinate would be taken as answering to movement of the north end of the magnet to the east. There is here however a little difficulty, which figure 5 will explain.

Fig. 5.

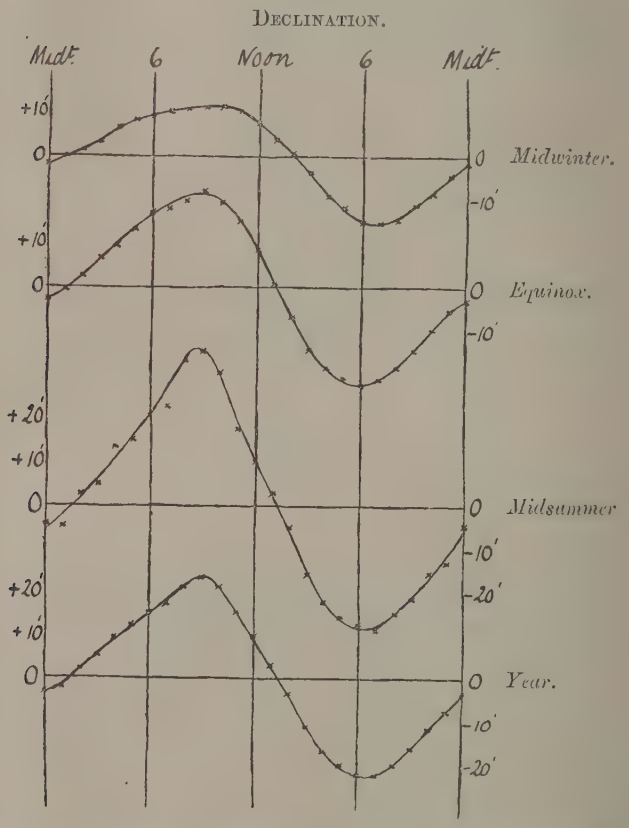


The 'Discovery's' "Winter Quarters" were to south-east of the south magnetic pole, so that the declination needle *ns* (*n* being the "north" pole) oriented itself as shown relative to the geographical meridian NS. If, following the usual practice, we define NO*n* as the declination (easterly), then an increase of easterly declination really means a movement of *n* towards the geographical west. In such a topsy-turvy state of matters one does not know what to expect the magnet to do. It has thus appeared simplest to take the positive direction of the ordinate as answering to increase in the declination angle NO*n*.

The two slides now to be shown (not reproduced) represent the regular diurnal variation of declination at Winter Quarters for each month of the year. To get smooth curves one would of

course require a good many years' data, but in every case the general character is quite clear. The range is 5 or 6 times as large as that at Kew. From May to July the sun was continuously below the horizon, but the diurnal range remained large, at least double that at Kew at midsummer. Another remarkable fact, the small seasonal change in the type of the diurnal variation, will be better seen in the next slide (fig. 6), which gives mean

Fig. 6.

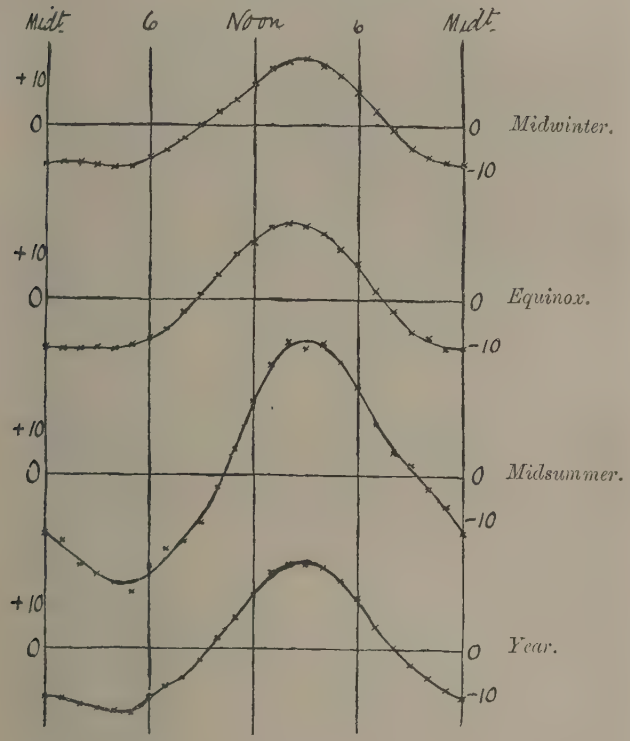


results for 3 seasons :—Midwinter (May to July), Equinox (March, April, September, October), and Midsummer (November to January), as well as for the whole year.

The curves pass through or close to all the observation points, and yet they are remarkably smooth. The way in which the "accidental" irregularities—*i. e.*, the disturbances which either have no period or a very long period—cut out is truly extraordinary. At some Arctic stations, observers have described a fundamental difference of type between the diurnal inequalities derived from

Fig. 7.

HORIZONTAL FORCE.



all and from quieter days. At "Winter Quarters" the regular diurnal inequality shows a decidedly reduced range on the quieter days, but the difference in type appears small. At Kew, and in temperate latitudes generally, as figs. 3 and 4 show, the changes of declination during the day are conspicuously larger

and more rapid than those during the night. At "Winter Quarters" there is no such conspicuous difference. Also the hours at which the extreme positions are reached, about 9 A.M. and 7 P.M., are so totally different from those customary, that it is difficult to say exactly wherein the Antarctic declination curves resemble and wherein they differ from those of temperate latitudes.

Fig. 8.

VERTICAL FORCE.

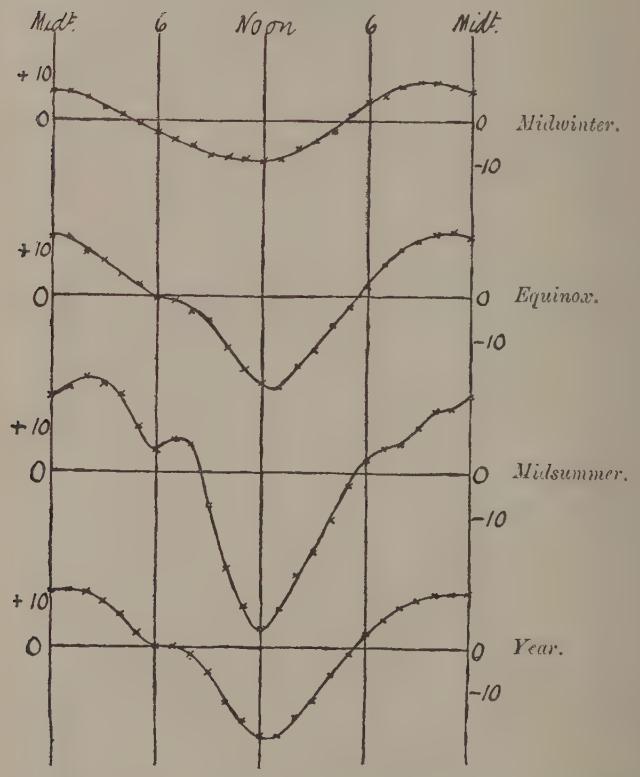


Fig. 7 illustrates the diurnal inequality of the horizontal force, *i. e.*, the variation in the intensity of the force directed along the local magnetic meridian. The positive direction of the ordinate means an increased value of the force; the unit, 1 γ, represents ·00001 C.G.S. The horizontal force at "Winter Quarters" was

little over a third of that at Kew, but the range of the diurnal inequality at Winter Quarters is at least 50 per cent. greater than that at Kew, whether at midwinter or midsummer. The type of the inequality again varies but little with the season, and is quite unlike that at any temperate station.

Fig. 9.

INCLINATION.

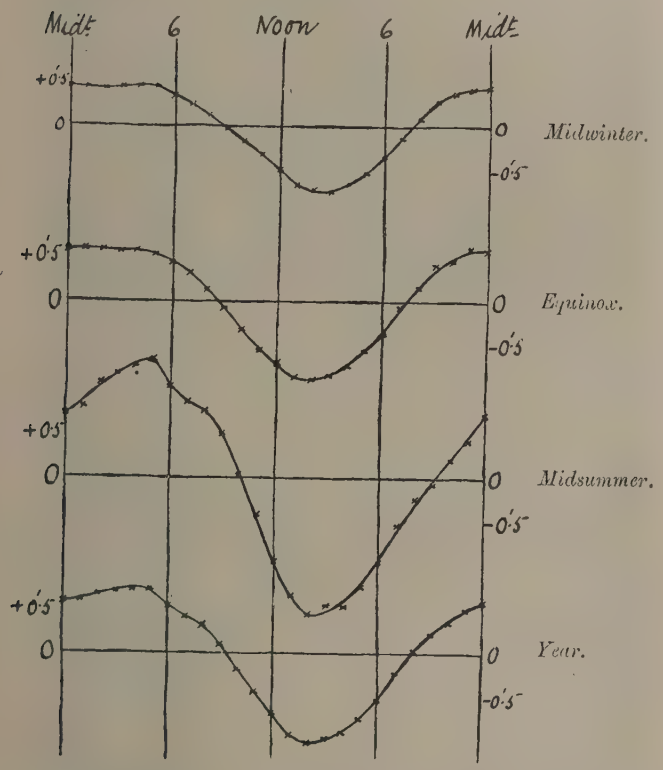


Fig. 8 illustrates the diurnal inequality of the vertical force. The unit again is 1 γ, and the positive direction of the ordinate answers to increasing force. The vertical force of course in the Antarctic pulls the *south* pole of a dipping needle downwards. The range is on the whole slightly less than in the case of the horizontal force, but quite double that at temperate stations in

Europe. It should, however, be mentioned that at "Winter Quarters" the vertical force is fully 10 times the local horizontal force, and more than 60 per cent. larger than that at Kew, so that compared to the size of the element the range of the vertical force at "Winter Quarters" is not so noteworthy.

There is some little apparent difference in type in the vertical force diurnal inequalities at different seasons. The kink, however, in the early morning part of the midsummer curve may be at least in part "accidental," as it occurs during those hours of the day when disturbances were most prominent. For most months of the year one had records for two years 1902 and 1903, but for the three midsummer months practically only from one year.

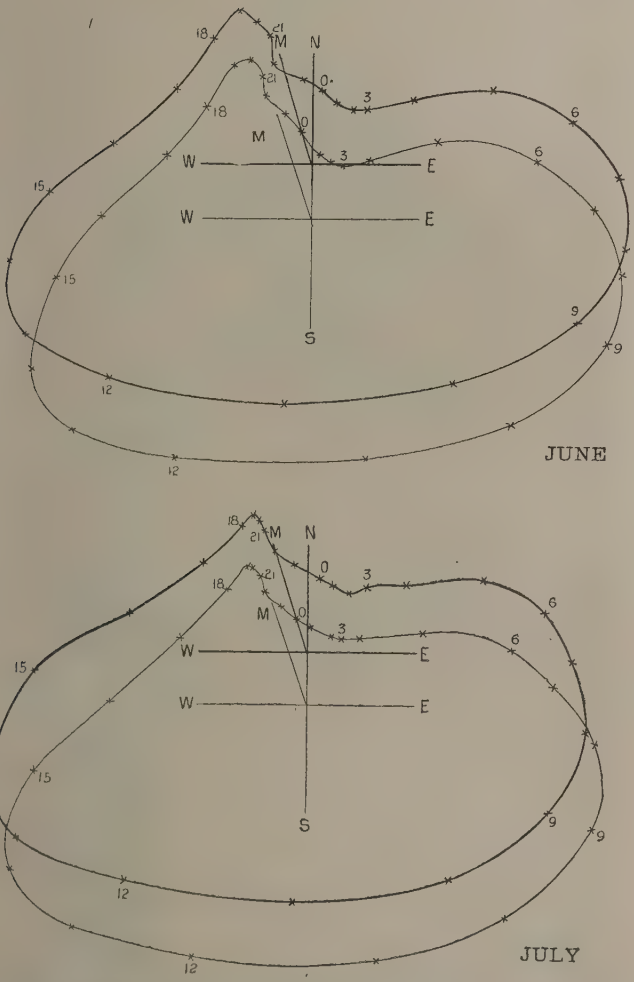
Fig. 9 illustrates the diurnal changes in the inclination as calculated from the corresponding changes in horizontal and vertical force. Increasing positive ordinate answers to increase of (Southerly) dip. The "Winter Quarters" was at no very great distance from the S. magnetic pole. The daily range however in the dip is by no means abnormally small, being in fact over 50 per cent. larger than at Kew. Whether the bend near 6 A.M. in the curve for midsummer is really representative, or is merely the product of "accidental" disturbances, it is difficult to say.

The last group of slides are of a different type. They are what are called "vector diagrams." Fig. 10—copied from the Phil. Trans. A, vol. 204, 1905—gives side by side vector diagrams for Kew (thicker lines) and Falmouth (thinner lines), for each of two midsummer months. The object of showing the curves for the two places is to emphasise the fact that the type of a vector diagram does not under normal conditions vary rapidly with longitude. Kew an inland station and Falmouth on the sea-coast differ notably in the diurnal variation of meteorological elements such as temperature (near the earth's surface), but so far as changes of terrestrial magnetism are concerned the differences are small.

Leaving now the Falmouth curves alone, let us concentrate our attention on the Kew curves, taking say for illustration that for June. The line drawn from the origin—where the north-south and east-west coordinate axes cross—to say the point 12 on the curve represents in magnitude and direction a disturbing force which would account for the observed departures in the horizontal components of the magnetic force at the hour 12 (noon) from their mean values for the day. Supposing, for instance, that the diurnal inequality were entirely due to electric currents in the

atmosphere, this line represents the horizontal component of the magnetic force exerted by these currents at noon at the earth's

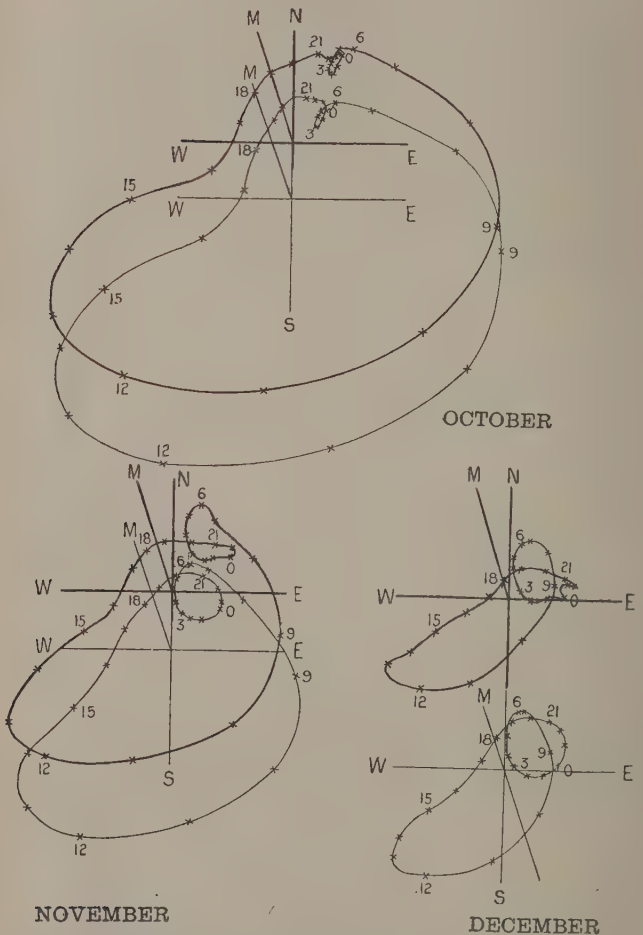
Fig. 10.



surface. N.S. and E.W. represent the geographical north-south and east-west directions, the line to M the local magnetic meridian.

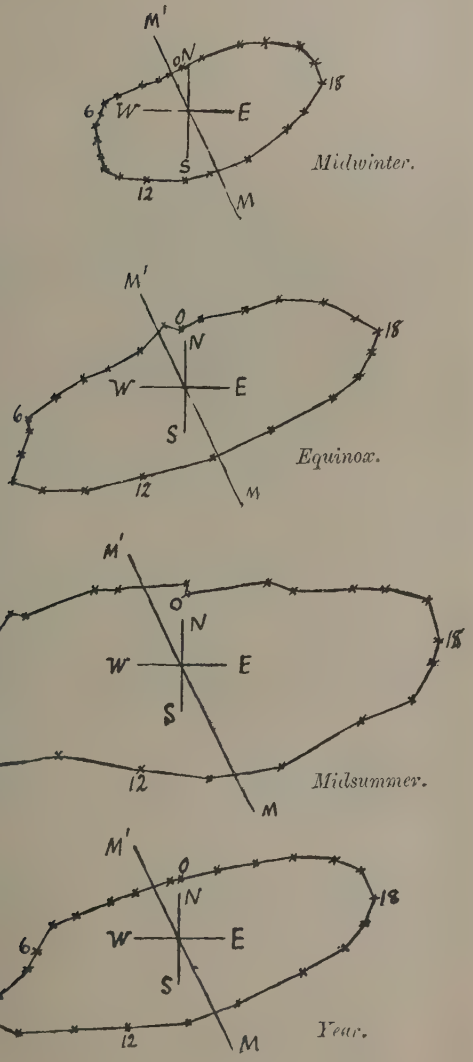
The hours are counted from 0 (midnight) to 23. The disturbing force, it will be seen, goes right round the compass in 24 hours, travelling in the direction of the hands of a watch. The force is

Fig. 11.



much larger, and changes its direction much more rapidly, by day than by night. The season chosen is that when the curve is most symmetrical, but even at midsummer its asymmetry is considerable. The next slide (fig. 11) shows the October, November, and

Fig. 12.


M'
0
N
18
6
W
E
S
12
M
Midwinter.
M'
0
N
18
W
E
6
S
12
M
Equinox.
M'
0
N
18
6
W
E
S
12
M
Midsummer.
M'
0
N
18
6
W
E
S
12
M
Year.

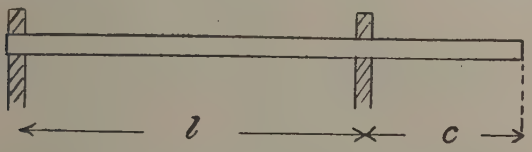
December vector diagrams, again for Kew and Falmouth. If the Falmouth diagram did not serve to corroborate, one might well hesitate to accept the Kew diagram for December as bearing even a distant resemblance to the actual facts. As we approach midwinter, a loop appears in the part of the diagram answering to the night hours. This really arises from the fact that the diurnal inequality has at most places an important 12-hour component, and at Kew this is able to assert itself prominently at midwinter. The scale of force is exactly the same in figures 10 and 11. The distances of the points marked N, E, S, and W from their corresponding origin represent in all cases 10 γ.

This will help to bring home the fact of the great increase in the intensity of the forces to which the regular diurnal inequality at a temperate station is due as we pass from midwinter to midsummer.

The next and last slide (fig. 12) gives vector diagrams for "Winter Quarters" for the whole year and the same three seasons as in figs. 6 to 9. As in figs. 10 and 11, NS and EW are drawn in and perpendicular to the geographical meridian. MM' represents the magnetic meridian, the north pole of the magnet pointing towards M. The distance from the origin to N, E, S, or W is 10 γ. The hours 0 to 23 are counted from midnight. It will at once be seen that there are remarkable differences from the phenomena at Kew and Falmouth. Seeing that we are dealing in fig. 12 with a station in the Southern hemisphere, the fact that the direction of motion is anti-clockwise is not to be regarded as an anomaly, though it might have been an unsafe *à priori* conclusion. But, for one thing, there is much less a-symmetry than in England. Again, the diagrams for the different seasons differ but little in type; and the differences, as regards amplitude and rate of motion of the radius vector, between the "day" and "night" hours are relatively inconspicuous. From a mathematical standpoint the most striking peculiarity in the diurnal inequality in the Antarctic in all the elements is the large size of the fundamental or 24-hour Fourier "Wave" as compared to the harmonics of shorter period.

VII. *On the Lateral Vibration of Bars supported at Two Points with One End overhanging.* *By* JOHN MORROW, *M.Sc., D.Eng.; Lecturer in Engineering, Armstrong College (University of Durham)* *.

WHEN a bar is carried on two supports and has one end overhanging by an amount c, as shown in the figure, its



natural period of vibration is to be determined from the equation

$$(\cosh ml \sin ml - \sinh ml \cos ml)(\cosh mc \sin mc - \sinh mc \cos mc) - 2 \sinh ml \sin ml (1 + \cosh mc \cos mc) = 0,$$

in which

$m = (2\pi N)^{\frac{1}{2}} (\rho\omega/EI)^{\frac{1}{4}}$;
E = Young's Modulus for the material;
I = the moment of inertia of the section about an axis perpendicular to the plane of bending;
ω = sectional area of bar (assumed uniform);
ρ = density of material;
N = frequency of natural vibrations.

For given ratios c/l we can obtain values of ml from the above equation. This has been done incidentally by Professor Dunkerley in connexion with his work on the whirling of shafts †, but the calculations were not sufficiently extended to give very accurate results. By comparison with the table given below, it will be seen that the approximate formula used by Dunkerley cannot be relied on to give more than the first two significant figures.

Having recently required more accurate solutions, I have

* Read November 8, 1907.
† Phil. Trans. A, 1894, p. 279.

found it necessary to make a more elaborate calculation, and as the results have been obtained to six figures it appears desirable to place them on record.

If we write a for c/l and θ for ml, and expand each term of the equation in ascending powers of θ and $a\theta$, we get, as far as the twenty-first powers,

$$4\theta^2-(\cdot0\dot4+\cdot\dot4\,a^3+\cdot\dot3\,a^4)\theta^6+(\cdot000035273369+\cdot00\dot21\dot64\,a^3 + \cdot00\dot3\dot7\,a^4+\cdot00\dot21\dot64\,a^7+\cdot000\dot79365\,a^8)\theta^{10}-(\cdot58730+ 106\cdot8890\,a^3+293\cdot945\,a^4+1007\cdot811\,a^7+881\cdot834\,a^8+ 106\cdot889\,a^{11}+26\cdot722\,a^{12})10^{-8}\theta^{14}+(\cdot033+13\cdot2\,a^3+49\,a^4 + 508\cdot8\,a^7+700\,a^8+509\,a^{11}+297\,a^{12}+13\cdot2\,a^{15}+2\cdot4\,a^{16})10^{-11}\theta^{18} =0.$$

Assuming values of a and calculating θ we obtain the numbers tabulated below:—

Ratio c/l.	Value of θ.
Unity	1·50592
Three-quarters ..	1·90170
One-half	2·51895
One-third	2·94042
One-quarter	3·05881
One-fifth	3·09975
One-sixth	3·11752
One-seventh	3·12647
One-eighth	3·13148
One-ninth	3·13449
One-tenth	3·13641
Zero	3·14159

Dr. Chree has given the following approximate formula for use when c/l is small *:—

$$ml=\pi(1-\tfrac{1}{6}\pi^2\,c^3/l^3).$$

It is stated to be satisfactory so long as $(c/l)^3\pi^3/6\coth\pi$ is small compared with unity. As a matter of fact we find

* Phil. Mag. [6] vol. vii. p. 517, May 1904.

that, when c/l is one-sixth, Chree's formula is correct to within 0·005 per cent., and the error is less than one per cent. even when c/l is one-half.

The number of vibrations per second is given by the formula

$$N = \frac{\theta^2}{2\pi}\sqrt{\frac{EI}{\rho\omega l^4}}.$$

September 1907.

VIII. *On the Contact Potential Differences determined by means of Null Solutions.* *By* S. W. J. Smith, *M.A.*, *and* H. Moss, *B.Sc.*, *Royal College of Science, London* *.

§ 1. Introduction.
§ 4. Palmaer's "null solutions."
§ 7. A method of search for other null solutions.
§ 9. Null solution of KCN.
§ 12. Effect of Na_2S upon the p.d. between Hg and KCl.
§ 16. Null solution of KCl.
§ 17. Effect of oxygen upon Paschen's relation.
§ 18. Inferences from results obtained with null solutions of KCN and of KCl.
§ 19. Null solution of KI.
§ 20. Null solution of KOH.
§ 21. Summary of conclusions.

§ 1. *Introduction.*—The processes which occur during the polarization of electrodes are of considerable theoretical and practical importance. Being largely surface effects, they can be followed, in the case of mercury, by observation of the changes of the surface-tension which result from polarization. Mercury electrodes have been the subject of much study in this way, but while the interpretation of some of the results seems clear, there are others which have been the subject of frequent discussion. Chief amongst these is the significance of the maximum surface-tension between mercury and the electrolyte which occurs at some particular degree of polarization in almost every solution that has been examined. The maximum was for long supposed to indicate

* Read February 28, 1908.

zero potential-difference between the mercury and the solution ; but the adequacy of this hypothesis, as a general interpretation of the significance of the maximum, is now very doubtful.

§ 2. Evidence was given by one of us (Phil. Trans. A. 1899, pp. 47–87), in discussing the validity of the Lippmann-Helmholtz theory of electrocapillarity, that the maximum surface-tension between mercury and certain electrolytes is not reached when the potential-difference is zero. It was shown that, for equally concentrated solutions of the particular electrolytes KCl and KI, the potential-differences at the respective maxima differ to such an extent that if one is assumed to be zero the other must be nearly a quarter of a volt (*l. c.* pp. 70, 71). The assumption of zero potential-difference in either case is arbitrary. It is possible that the potential-difference at the maximum surface-tension is zero in some electrolytes; but the evidence from the electrocapillary curves (*l. c.* pp. 68 & 82), while not conclusive, favours the view that it is not so in any of the moderately dilute solutions of KCl and KI (giving "depressed" maxima) referred to above.

Palmaer has, however, published experiments recently from which it would seem that in the case of $n/10$ KCl, the potential-difference at the maximum surface-tension is, if not zero, at least very small. This result, if conclusive, would be of great theoretical value, and we have therefore performed the experiments described below to test the validity of Palmaer's deductions.

§ 3. Palmaer published in 1903 (*Zeitsch. f. Elektrochemie*, ix. pp. 754–757) a summary of certain experiments with drop electrodes, by means of which he sought to show that the true contact potential-difference between mercury and $n/10$ KCl solution is about 0·57 volt, and he has quite recently (*Zeitsch. f. physik. Chemie*, lix. pp. 129–191, 1907) given a full account of these experiments and of others, from which his final conclusion is that the potential-difference in question is $0{\cdot}5732 \pm {\cdot}0003$ volt at 18° C.

One of us found that the maximum surface-tension between

mercury and $n/10$ KCl solution was produced by a polarizing electromotive force of $0{\cdot}568 \pm {\cdot}01$ volt (*l. c.* p. 71). It would thus appear that, after all, in the case of $n/10$ KCl, the potential-difference at the maximum surface-tension is practically zero, for it is represented by the difference between the two numbers just given. We shall attempt to show however that, although of much interest in connexion with electrocapillarity, Palmaer's deduction from his experiments is not necessarily true, and that his results leave the knowledge of the contact potential-difference between Hg and $n/10$ KCl substantially in the same state of uncertainty as before.

§ 4. *Palmaer's Null Solutions.*—When certain conditions, first fully discussed by Paschen, are fulfilled, a mercury electrode immersed in $n/10$ KCl shows a potential about $0{\cdot}57$ volt higher than that of an electrode of mercury streaming into the same solution. Palmaer found that by adding certain substances to this $n/10$ KCl solution, he could not only reduce the observed potential-difference between the still and dropping mercury until it became very small, but could cause it, passing through the value zero, to change in sign. In this way he found two different "null solutions," one containing small quantities of KCN, KOH, and $Hg(CN)_2$, and the other H_2S and a small quantity of acetic acid, for which the potential-difference between the still and dropping electrodes was zero. It is of course well known that a concentrated solution of a mercury salt behaves like a Palmaer null solution in the respect that there is practically no p.d. between still and dropping mercury electrodes immersed in it; but small variations in the composition do not here produce effects of the kind observed by Palmaer. Moreover, the absence of a p.d. in this case has been explained in a way which is not applicable when the amount of dissolved mercury is very small.

§ 5. Experiments of the kind performed by Palmaer were suggested by Nernst (*Ann. d. Physik*, lviii. p. 11, 1896), and it is obvious that the results can be explained, either according to the Helmholtz theory of dropping-electrodes or

to that of Nernst, if we assume that when the observed E.M.F. is zero a solution has been found which exhibits no potential-difference with respect to mercury. In such a case there would be no tendency to produce an E.M.F., whether, in the general case, the double-layer potential is altered by extension of the mercury surface (Helmholtz), or whether the double-layer forms practically instantaneously but is accompanied by concentration changes in the solution (Nernst).

§ 6. Connecting each of his null solutions in turn to a solution of $n/10$ KCl, Palmaer measured the p.d. between mercury in the null solution and mercury in the $n/10$ KCl. Allowing for small contact potential-differences between the electrolytes, he found practically identical values (of which the mean is the number already quoted) for the p.d. Hg | $n/10$ KCl. Strictly, these measurements prove only that the p.d. between mercury and each of the null solutions was the same.

Palmaer found only two satisfactory null solutions; but experiments with several others are described below. From these experiments it will be seen that the p.d. between mercury and a null solution of the type described by Palmaer is not always the same, and hence is never necessarily zero as Palmaer assumes.

§ 7. *A method of search for other Null Solutions.*—In searching for other null solutions we were guided by the relation deducible from Paschen's experiments, that although the p.d. between Hg and an electrolyte when the surface-tension is a maximum need not be zero, it is nevertheless always equal to the p.d. between a dropping electrode of the Paschen type (Wied. *Ann.* xli. p. 42, 1890) and the same electrolyte (*cf.* Phil. Trans. *l. c.* pp. 83 *et seq.*). We have found, in the course of the present experiments, that the statement of this relation, which is one of the most important in electrocapillarity, requires qualification. The relation is true only when the medium through which the mercury falls before it enters the solution does not contain a constituent which interacts chemically with the mercury and the solution. In some cases, for example, the relation does not hold until

the air surrounding the dropping electrode and the solution is replaced by hydrogen, nitrogen, or other non-oxidising medium.

§ 8. Assuming the truth of the above relation, it was obvious that any solution for which the maximum of the electrocapillary curve lay at the origin (applied E.M.F. zero) would be a null solution. If the maximum for a given solution were slightly (*a*) to the right or (*b*) to the left of the origin, then the still electrode for that solution would be slightly (*a*) positive or (*b*) negative to the dropping electrode. The change in sign of the potential of the dropper with respect to the still electrode, with a small change in the composition of the electrolyte, would not correspond necessarily (as assumed by Palmaer) with a change in the sign of the potential of the still mercury with respect to the solution, but only with a change from one side of the origin to the other of the maximum of the electrocapillary curve.

Since it is almost certain that this maximum does not always correspond with zero potential-difference, it seemed equally certain that a null solution of the kind studied by Palmaer could not always, and need not ever, be one exhibiting no contact p.d. with respect to mercury.

§ 9. *Null Solution of* KCN.—It has long been known that moderately concentrated solutions of KCN give electrocapillary curves of which the maxima lie to the left of the origin (applied E.M.F. negative), while weaker solutions give curves of which the maxima lie to the right. If a solution could be found of which the maximum lay at the origin, this would be a null solution of the kind studied by Palmaer. A null solution of KCN was apparently found approximately by Amelung in a research which Palmaer describes (*Zeits. f. physik. Chemie*, lix. p. 164, 1907) but regards as unsatisfactory. This solution used according to Palmaer's method would give a value of roughly 0·7 volt for the contact potential Hg | *n*/10 KCl. It was obtained by gradual dilution of a saturated solution of KCN until the p.d. between the drop electrode and the still electrode became zero.

We have found and examined a null KCN solution in another way. A normal solution of KCN was made up and this, together with weaker solutions of definite strength, obtained from it by dilution, was then examined as described below. As it was found that the electrocapillary properties of solutions, apparently of equal concentration, produced from different samples of KCN frequently differed considerably, the precise constitutions of the different solutions cannot be specified. This, however, is of no importance to the validity of the experiments. For the sample of KCN used in the experiments, the null solution contained about 0·26 *n* KCN; but another sample from another source would probably have given a different result.

The following quantities were observed in the case of each solution:—

1. The electrocapillary curve—the reading for maximum surface-tension, and the E.M.F. required to produce it, being noted as carefully as possible.

2. The electrocapillary curve of a solution of KCl of equal strength.

3. The horizontal distance between the descending branches of the two curves (*cf.* Phil. Trans. *l. c.* p. 69).

4. The E.M.F. of the cell $\mathrm{Hg} \mid \mathrm{KCN} \vdots \mathrm{KCl} \mid \mathrm{Hg}$.

5. The E.M.F. of the dropping electrode circuit $\mathrm{Hg} \downarrow \mid \mathrm{KCN} \mid \mathrm{Hg}$, the measurements being taken when the end of the continuous part of the jet was in the surface of the solution (Paschen).

6. The E.M.F. of the dropping electrode circuit $\mathrm{Hg} \downarrow \mid \mathrm{KCN} \vdots \mathrm{KCl} \mid \mathrm{Hg}$.

Some of the electrocapillary curves are shown in fig. 1, the others being omitted to avoid confusion. The KCN curves are very flat near the maxima, and the E.M.F.s corresponding to these maxima are relatively difficult to determine.

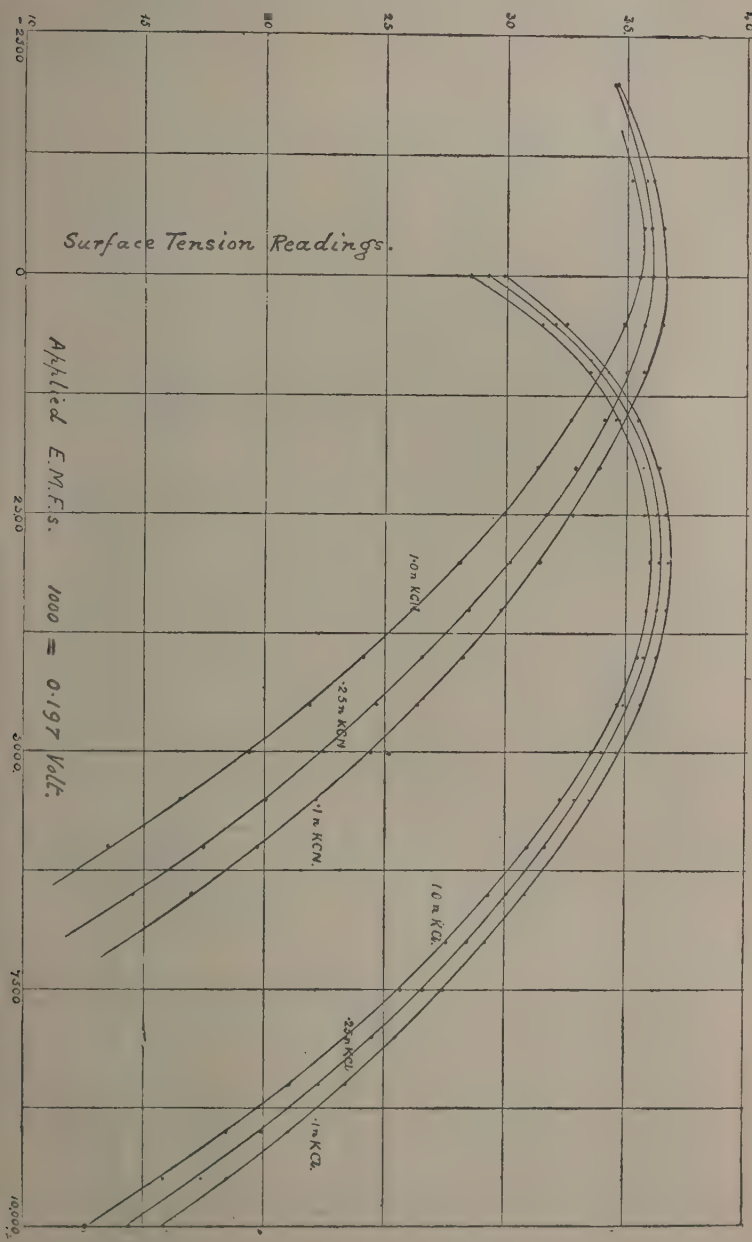

Surface Tension Readings.
Applied E.M.Fs. 1000 = 0·197 Volt.
1·0 n KCN.
·25 n KCN.
·1 n KCN.
1·0 n KCl.
·25 n KCl.
·1 n KCl.

Fig 1.

The chief results of the measurements are summarized in the following Table:—

	1.	2.	3.	4.	5.	6.	7.
Strengths of solutions.	Max. S.T. KCN (scale-reading).	Max. S.T. KCl (scale-reading).	E.M.F. of Max. S.T. KCN volt.	Horizontal distance between curves. volt.	KCN | KCl + volt.	KCN + volt.	KCN | KCl + volt.
0·1 *n*.	36·65	36·75	·039	·645	·642	·043	·679
·2 *n*.	36·30	36·70	·020	·667	·671	·018	·694
·24 *n*.	36·10	36·53	·010	·687	·687	·012	698
·25 *n*.	36·08	36·35	0	·691	·690	·003	·699
·26 *n*.	36·04	36·30	0	·696	·693	−·001	·697
·27 *n*.	36·00	36·27	−·005	·697	·696	−·005	·693
·50 *n*.	35·81	36·17	−·020	·716	·715	−·016	·703
1·0 *n*.	35·70	36·10	−·059	·748	·745	−·046	·705

Solutions of KCN and KCl of equal strength being of approximately the same conductivity and degree of ionization (*cf.* Kohlrausch & Holborn, *Leitvermögen der Elektrolyte*, pp. 145 & 148), the contact potential-difference between them will be very small, probably less than a millivolt. This is confirmed by the agreement between the numbers in Columns 4 and 5, since the former represents the difference between Hg | KCl and Hg | KCN (*cf.* Phil. Trans. *l. c.* pp. 69 *et seq.*).

Each number in Column 7 should be equal to the sum of the corresponding numbers in Columns 5 and 6. A comparison serves to indicate the limits of the uncertainty of the dropping-electrode measurements. The jet fell freely in contact with the air. By comparison of the numbers in Columns 3 and 6 it will be seen that Paschen's relation held, within the limits of errors of experiment, in every case.

The null solution was that for which the surface-tension was a maximum in the natural state (applied E.M.F. zero). Its strength was, in round numbers, $n/4$ KCN, and assuming with Palmaer that, in consequence, Hg | $n/4$ KCN = 0, it would give, by Column 5, Hg | $n/4$ KCl = 0·69 approximately.

§ 10. As will be seen later, a solution of $n/4$ KCl, examined according to either of the methods described by Palmaer, would have given a null solution from which he would have deduced the value Hg | $n/4$ KCl = 0·565 approx.

The reason of the difference of 0·125 volt between this and the value found by the KCN null solution is suggested by inspection of the electrocapillary curves.

The maxima for the KCN solutions are lower than those for the KCl solutions of corresponding strength, and the "horizontal distance" between the curves after they become parallel is approximately 0·125 volt greater than the distance between the maxima. Consequently (*cf.* Phil. Trans. *l. c.* p. 67) the solution at the maximum surface-tension in KCN is 0·125 volt more positive to the mercury than it is at the maximum in KCl.

§ 11. Every solution for which the maximum of the electrocapillary curve is at the origin is a null solution, but the potential-differences between mercury and different null solutions will be different if the maxima for these solutions are not the same.

If traces of other substances can be added to a $n/4$ KCl solution in such a way as to move the maximum of the electrocapillary curve to the origin without appreciably raising or depressing it, then such a solution will be about 0·125 volt less positive to mercury than the null solution of $n/4$ KCN. This null solution when measured against pure $n/4$ KCl will give an E.M.F. of 0·565 in place of the E.M.F. of 0·69 given by the $n/4$ KCN null solution. Hence, if Palmaer's solutions were produced from $n/10$ KCl without appreciable alteration of the maximum, the difference between his results and ours is immediately explained.

§ 12. *Effect of* Na_2S *on the p.d. between* Hg *and* KCl.—The p.d. between mercury and an electrolyte is controlled, according to the theory of Nernst, by the concentration p of the mercury ions in solution. If π is the potential rise from the solution to the mercury, then

$$\partial\pi/\partial p = k\mathrm{T}/p, \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}^*$$

where T is the absolute temperature and k is a constant. The rise can therefore be diminished by decreasing p. From Palmaer's experiments and others (*e. g.*, Behrend, *Zeits f. phys. Chem.* xi. p. 481, 1893), it can be inferred that a large diminution of p is produced by saturating a KCl solution in

* An interesting method of deducing a similar equation was given by Professor J. J. Thomson in the Philosophical Magazine for 1895.

contact with mercury with H_2S. We therefore thought it likely that by addition of Na_2S to the KCl solution it would be possible to move the electrocapillary curve to the right, *i. e.* so that the maximum approached the origin. It remained to determine by experiment the relative amount of Na_2S necessary for the purpose of reaching the origin. Electrocapillary curves were obtained with solutions containing gradually increasing proportions of Na_2S. The general composition of the solutions was

$$x(n\,\mathrm{KCl}) + y(n\,\mathrm{Na_2S},\,9\mathrm{H_2O}),$$

where $x+y=0{\cdot}1$; *i. e.*, considering the sum of the contents, the solution was always 1/10th normal, and the content in kations remained approximately constant. Curves were obtained for a number of different values of y. Some of the results are shown in fig. 2, in which the values of y represented are as follows:—

No. of Solution ...	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XIII.	XV.
Value of y	0	$\cdot0_2$	$\cdot0_3372$	$\cdot0_3374$	$\cdot0_3377$	$\cdot0_21$	$\cdot0_22$	$\cdot0_25$	$\cdot01$	$\cdot03$	$\cdot08$	$\cdot10$

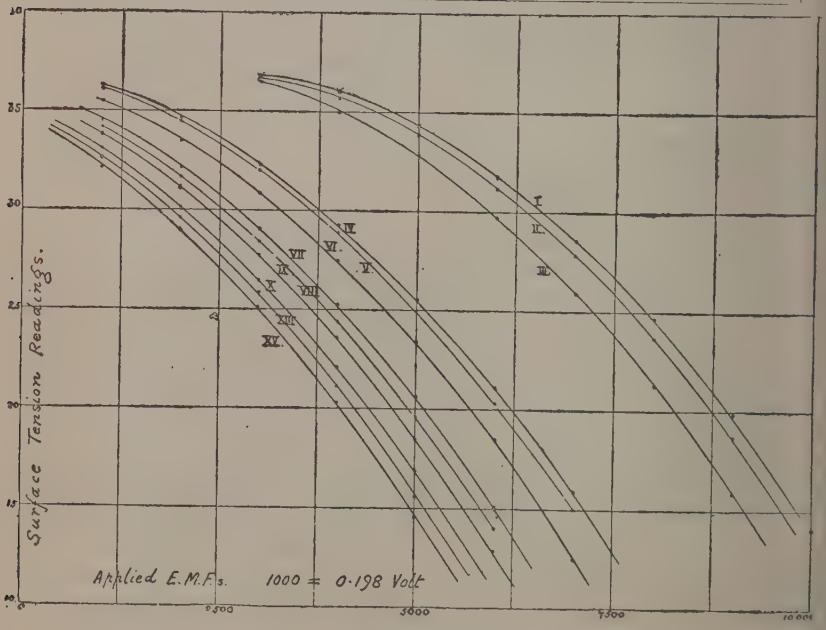
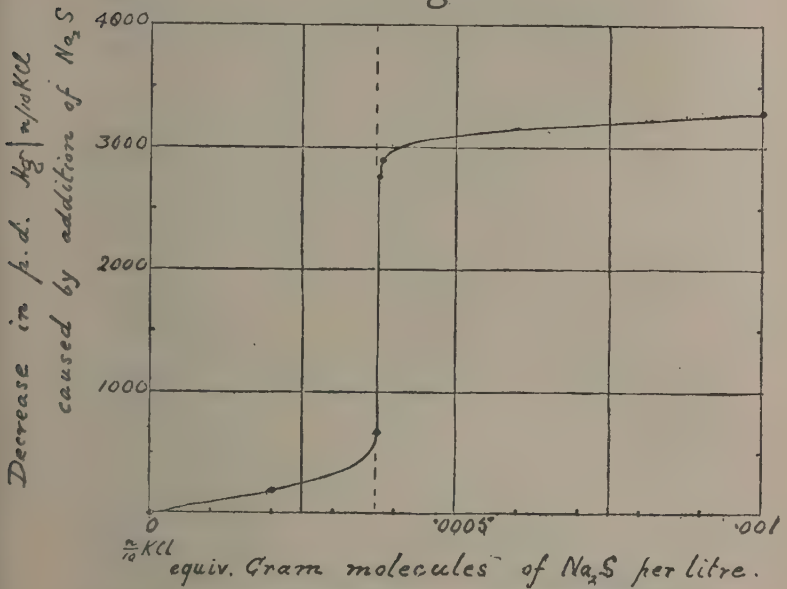


Fig. 2

From these results it will be seen that less than ·001n Na_2S added to ·099n KCl was sufficient to move the maximum of the electrocapillary curve to the left of the origin. Further, when the value of y was about ·00037, an extremely small variation produced a very large change in the position of the maximum. This is represented in fig. 3, which shows how the displacement of the descending branch of the electrocapillary curve depends on the percentage composition of the $n/10$ solution. Since the concentration in kations was the same for all solutions, this curve represents (Phil. Trans. *l. c.* p. 80) how the potential of the solution with respect to the mercury rises with increase in the amount of the sulphide.

Fig 3



§ 13. The extremely rapid concentration variation of the potential near $y=$·00037 was very inconvenient for our purpose, for it happened that the solution which we sought, *i. e.* one having its electrocapillary maximum at the origin, would contain an amount of sulphide corresponding approximately to this value of y. The experiments of Behrend

(*l. c.* p. 481) suggested that the rapid variation of potential at a critical value of y occurred near the completion of the conversion of feebly soluble chloride of mercury into still less soluble sulphide. Thus, assuming c to represent the concentration of Hg_2Cl_2 in solution before addition of Na_2S, if the amount of sulphide added were $(c-c')$, *i. e.* less than c, we might have (see however § 15) :—

$$cHg_2Cl_2+(c-c')Na_2S=c'Hg_2Cl_2+(c-c')Hg_2S \\ +2(c-c')NaCl.$$

Assuming α and β to represent the fractions of the chloride and sulphide respectively, which are electromotively active, the ionic concentration p of the mercury in solution would be

$$p=2\alpha c'+2\beta(c-c'), \quad \text{and hence} \quad \partial p/\partial c'=2(\alpha-\beta).$$

Then, from equation (i.) above, we should have

$$\partial\pi/\partial c'=k\mathrm{T}(\alpha-\beta)/(\alpha c'+\beta c-c').$$

From this it is seen that if β is very small compared with α, the value of $\partial\pi/\partial c'$ will become very large when c' becomes very small, *i. e.* when the amount of Na_2S added is very nearly equivalent to the amount of Hg_2Cl_2 in solution.

§ 14. When the amount of Na_2S added is in excess of the Hg_2Cl_2 in solution we may have

$$cHg_2Cl_2+(c+c')Na_2S=cHg_2S+c'Na_2S+2cNaCl.$$

From this it is seen that the potential of the liquid with respect to the electrode will continue to rise when, after the whole of the chloride is decomposed, more and more Na_2S is added. For, assuming the law of mass action, the ionic concentration of the Hg obtained from the Hg_2S will diminish when, by introduction of further quantities of Na_2S, the concentration of the S ions in solution is raised.

Suppose now that to a solution containing an excess of Na_2S a small quantity $2c''$ of an acid HX is added. Then we shall get

$$cHg_2Cl_2+(c+c')Na_2S+2c''HX \\ =cHg_2S+(c'-c'')Na_2S+c''H_2S+2c''NaX+2cNaCl.$$

Now if we assume the coefficients of ionization of the Na_2S and the H_2S to be γ and δ respectively, the concentration of S ions arising from these two substances will be $\gamma(c'-c'')+\delta c''$; while, before the addition of the acid, the concentration of S ions arising from the Na_2S would exceed $\gamma c'$. The value of δ will in general be less than that of γ, because, in moderately dilute solution, H_2S is a very poor conductor compared with Na_2S. Therefore addition of the acid HX will reduce the concentration of the S ions in the solution containing cHg_2S, and will in consequence cause the concentration of the Hg ions to rise. Thus addition of the acid will tend to reduce the effect of the Na_2S and will cause the electrocapillary curve to move towards the right.

Hence, if too much Na_2S has been added, so that the maximum is to the left of the origin, it may be possible to obtain a null solution by the addition of a small quantity of an acid. Moreover, it may be of advantage experimentally to proceed in this way by overshooting the mark and then adding acid, rather than by attempting to hit it by reducing the amount of Na_2S. For, as can be seen, the rate at which the curve will move towards the right will be less when a small quantity of acid is added than when an equivalent quantity of sulphide is taken away. Thus, when the acid is absent, the concentration p_s of S ions, outside the Hg_2S, is such that $\partial p_s/\partial c'$ exceeds γ; but when the acid is added

$$\partial p_s/\partial c''=-(\gamma-\delta).$$

§ 15. It is not contended for the above equations that they necessarily do more than indicate the course of events. The Na_2S used probably contained traces of higher sulphides, and the chemical relations between the substances concerned are complicated. The final product of the action of Na_2S on the mercury in solution would no doubt be a double sulphide of HgS and Na_2S, and it is worth notice with regard to this that, after the very rapid change at $\cdot00037n$ Na_2S, the potential of the electrode continued to decrease fairly rapidly until about $\cdot002n$ Na_2S had been added. The rate of decrease fell comparatively suddenly at this point, and for subsequent additions of Na_2S (until the whole of the KCl was replaced) remained very small.

The concentration of mercurous ions in a solution of KCl standing over mercury and calomel has been estimated indirectly by Behrend and others, and from the values obtained it would appear that, if the above interpretation of our observations is correct, only a small fraction of the mercury in solution can be in the ionized condition. It is important to note, however, that the comparatively large value of the solubility of Hg_2Cl_2, to which the results of § 12 seem to lead, may on account of the influence of dissolved atmospheric oxygen be more apparent than real. It is commonly agreed that the interaction between Hg and a solution of a chloride, from which the existence of Hg_2Cl_2 in the solution results, occurs through the intervention of the oxygen dissolved in the latter. This interaction will continue (1) until the solution becomes saturated with Hg_2Cl_2, or (2) until the supply of oxygen near the electrode is used up. In the latter event, further formation of Hg_2Cl_2 would cease until, by diffusion, a fresh supply of oxygen approached the electrode. Since, however, the solubility of oxygen in $n/10$ KCl is probably much greater than that of Hg_2Cl_2, it is probable that the interaction terminates in accordance with the first of the alternatives and before he whole of the oxygen per c.cm. near the electrode is removed. If now a small quantity of Na_2S is added to the solution it will precipitate the whole or a part of the Hg_2Cl_2 with which the solution is saturated. But the further solution of Hg_2Cl_2 will be possible by interaction between the mercury, the KCl in the solution and the excess of dissolved oxygen. In fact the complete removal of Hg_2Cl_2 from solution by means of Na_2S, as represented in the equations given in §§ 13, 14, will not be possible until the whole of the dissolved oxygen is used up.

From this point of view, what happens when an aerated solution of KCl containing Na_2S is poured upon mercury may be described, figuratively, as a competition between the salts for the oxygen and mercury in the surface layer. Since any Hg_2Cl_2 formed before the removal of the Na_2S is complete will be at once decomposed by the latter and precipitated as sulphide, the net result of this competition is that the KCl can only interact permanently with such oxygen as

the Na_2S leaves uncombined. The critical amount of the latter is reached when it leaves none *.

In any attempt to form a complete picture of the process, however, it would be necessary to take account of possible difference in the subsequent rates of approach of Na_2S and O to the surface layer, from above, by diffusion and convection. This would lead us too far from our present aim.

The exact composition of our critical Na_2S solution was uncertain, and the further study of the question presented chemical difficulties which it did not seem profitable to investigate with the materials at our disposal.

§ 16. *Null Solution of* KCl.—The argument developed above proved successful as a working hypothesis. An $n/10$ KCl solution containing $\cdot001n$ Na_2S was first made up, and others containing different amounts of acetic acid (suggested by Palmaer's experiments) were then obtained from it. The results of the experiments with these solutions are summarized below:—

1.	2.	3.	4.	5.	6.	7.
Strength of acetic acid.	Max. S.T. (scale-reading).	E.M.F. for Max. S.T. (volt.)	Horizontal distance to $\frac{n}{10}$ KCl curve.	sol. $\vert \frac{n}{10}$ KCl $\vert +$ (volt.)	$\downarrow$ sol. $\vert +$ (volt.)	$\downarrow$ sol. $\vert \frac{n}{10}$ KCl $\vert +$ (volt.)
0	36·82	−·123	·661	·660	−·129	·564
·0011 n	36·81	−·051	·622	·618	−·049	·560
·0017 n	36·84?	−·020	·588	·582	−·018	·564
·0023 n	36·80	−·005	·578	·571	−·009	·564
·0028 n	36·80	·010	·568	·562	·005	·562
·0040 n	36·80	·020	·556	·549	·016	·564

36·80 = Maximum S.T. for $n/10$ KCl.

The numbers representing the normality in acetic acid are only approximate. Nothing turns upon the accuracy of their

* Some results of experiments still in progress in connexion with this view were indicated when the paper was read.

determination. Some of the corresponding electrocapillary curves are shown in fig. 4.

The measurements are less exact than in the case of the KCN curves. Owing no doubt to the presence of small quantities of dissolved oxygen, the p.d. between the large Hg electrode and the solution sometimes changed perceptibly during the short time required to determine the electrocapillary curve. It will be seen, however, that a series of curves with practically equal maxima of surface-tension was now obtained. The null solution lies between IV. and V.,

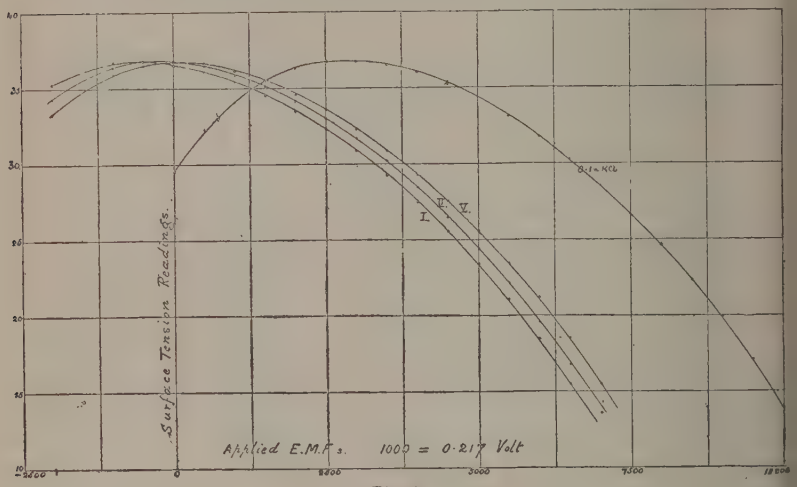


Fig. 4.

and corresponds within the limits of experimental error with a solution of which the maximum of the electrocapillary curve is at the origin. Part of the difference between the numbers in columns 4 and 5 was certainly due to increase with time of the p.d. Hg | solution. The capillary curves were taken first and are not exactly parallel to the decinormal KCl curve. The distance decreases slightly towards the lower ends of the curves. The p.d. between the strongest of the solutions and the $n/10$ KCl solution was probably less than a millivolt (*cf.* Palmaer, *Zeit. p. Chem.* l. c. 1907, p. 155).

By examination of the data for solutions IV. and V. it is seen that a null solution of the present kind, interpreted according to the assumptions of Palmaer, would give, for the p.d. Hg | $n/10$ KCl, a value agreeing with his result. But, as will be seen, his assumption of zero p.d. between Hg and the null solution is not at all necessary. The only necessary conclusion is that the p.d. between the still Hg and the solution is the same as that between the dropping Hg and the solution.

From the data in the Table it is seen that, for reasons already given, the maxima being practically equal in all the solutions, the p.d. between the dropping electrode and the solution should be in every case the same. This result is probably of significance in the theory of electrocapillarity. Its truth is shown by the practical equality of all the numbers in Column 7.

§ 17. *Effect of Oxygen upon Paschen's relation.*—With respect to the data in columns 3 and 6, § 16, showing the fulfilment of the Paschen relation for the present series of electrolytes, it is important to state that the dropping-electrode experiments were performed in an atmosphere of hydrogen (*cf.* § 7, above). A piece of wide glass tubing open at both ends encircled the dropping electrode. The lower end of this tube was immersed in the electrolyte, and the upper was closed by a rubber cork in which were three holes. The drop electrode passed through the central hole: the others served for the inlet and outlet of the hydrogen respectively.

The following data are given as examples of the necessity for the exclusion of air. In one case, the maximum of the capillary curve being +·01 volt, a Paschen electrode against still mercury in the same solution showed −·05 volt, increasing to −·07 when the mercury jet was partially immersed. The solution quickly became cloudy and the mercury tarnished so rapidly that it fell as a dirty powder.

In another experiment the jet was surrounded by hydrogen, the water used in preparing the solution having been recently boiled to decrease the amount of dissolved air. Before complete displacement of the air by hydrogen, the Paschen

electrode E.M.F. was −·024 volt. It fell gradually to −·014 volt and then remained constant. The mercury fell quite clean. Some of the solution was now withdrawn, and its electrocapillary curve was determined. The maximum lay at −·015 volt.

In a third experiment, the jet being surrounded by hydrogn, the electrode E.M.F. was −·024, agreeing with the electrocapillary maximum. Oxygen was now admitted and displaced the hydrogen. The Paschen electrode E.M.F. became −·140. With the jet partially immersed the E.M.F. increased to −·240.

Various experiments with other gases and with insulating liquids were tried, *e. g.*, it was found that the Paschen relation was, under certain conditions, fulfilled when air was replaced by benzene; but further description of these experiments is omitted from consideration of space.

§ 18. *Inferences from results obtained with Null Solutions of* KCN *and of* KCl.—Summarizing the results of the two series of experiments described, it is seen that, with respect to the p.d. Hg | electrolyte as considered by Palmaer, there are two kinds of null solution. One is formed by the addition to the electrolyte of very small quantities of certain substances which leave the shape of the electrocapillary curve unaltered, with the maximum undepressed, but move it parallel to itself towards the left. This kind of null solution, interpreted in the way described by Palmaer, will give the result that the p.d. is zero at the maximum of the electrocapillary curve.

A second kind of null solution is obtained by using a different electrolyte and altering its concentration until the maximum of the capillary curve is at the origin. This kind may have a depressed maximum compared with the original electrolyte, KCl for example, and will in that case give a value, for the p.d. Hg | KCl, greater than that obtained by Palmaer if the measurements are interpreted in the way he describes. If, on the other hand, the curve for the null-solution electrolyte has a higher maximum than the corresponding curve for KCl, then the p.d. Hg | KCl found by Palmaer's method will be less than that which he gives.

We have not attempted to find a null solution exactly of this last kind, although it is known that the electrocapillary maximum of a saturated KOH solution is near the origin and is considerably higher (Phil. Trans. *l. c.* p. 68) than that of concentrated KCl.

We have, however, obtained null solutions by the addition of small quantities of Na_2S (and acetic acid) to $n/10$ KI solution, which has a very depressed maximum, and to $n/10$ KOH solution, which has a higher maximum than $n/10$ KCl. The results of these experiments exhibit the truth of the conclusions we have drawn.

§ 19. *Null Solution of* KI.—The attempt to obtain a null solution from $n/10$ KI succeeded approximately when the composition of the solution was about $\cdot001n\,Na_2S + \cdot099n$KI. The maximum surface-tension occurred when the applied E.M.F. was $-\cdot01$ volt. It was unnecessary for our purpose to obtain a nearer approximation to a null solution. The E.M.F. between a dropping electrode falling through hydrogen into this solution and a still electrode was at first imperceptible. After some time it was ·006 volt. Mercury in this solution measured against mercury in $n/10$ KCl gave an E.M.F. of ·793 volt. A fresh null solution of KCl, made up by trial for comparison, measured against $n/10$ KCl in the same way gave ·565 volt. The two solutions measured against each other gave ·228 volt. The results of the measurements are tabulated below:—

1.	2.	3.	4.	5.	6.	7.
Null Solution.	Max. S.T. (scale-reading).	E.M.F. for max. S.T.	Horizontal distance to $\frac{n}{10}$ KCl curve.	sol. | $\frac{n}{10}$ KCl | +	sol. | +	null KI | null KCl | +
		volt.	volt.	volt.	volt.	volt.
$\frac{n}{10}$ KI + $\frac{n}{1000}$ Na_2S	28·85	$-\cdot01$	·789	·793	0	·228
$\frac{n}{10}$ KCl + $x$$Na_2S$ ...	30·5	$-\cdot01$	·569	·565	$-\cdot01$	

These experiments show that the p.d. Hg | $n/10$ KCl cannot be 0·57 unless, interpreting them according to Palmaer's method, the p.d. between $n/10$ KCl and $n/10$ KI is nearly a quarter of a volt. Such a potential-difference is impossible according to the theories at present in vogue (*cf.* Phil. Trans. *l. c.* p. 62).

§ 20. *Null Solution of* KOH.—In attempting to obtain a null solution from $n/10$ KOH it was found that the addition of Na_2S ($\cdot 001n$ to $\cdot 002n$) produced a gradual shift of the maximum to the left which continued over a long time. A solution with the maximum at the origin could not be obtained conveniently with Na_2S alone on account of this time effect It was found however that if, after the solution had stood for some time over the mercury, dilute acetic acid was added drop by drop and the solution stirred, the maximum could be brought from the left to zero and the time effect was now negligible. The results of the experiments with this null solution are given below :—

1.	2.	3.	4.	5.	6.
Null Solution.	Max. S.T. (scale-reading).	E.M.F. for max. S.T. volt.	Horizontal distance to $\frac{n}{10}$ KCl curve. volt.	null sol. | $\frac{n}{10}$ KCl | + volt.	null sol | + volt.
$\frac{n}{10}$ KOH + Na_2S + $HC_2H_3O_2$	30·61	+·01	·515	·509	·008

In considering the value 0·509 volt in column 5 it has to be remembered that there is now an appreciable p.d. between the solutions. Its value calculated in the usual way is $n/10$ KOH | $n/10$ KCl = ·016 volt at 20° C.; and consequently we now obtain, according to Palmaer's method, Hg | $n/10$ KCl = ·525 volt. But, according to the interpretation we have offered, this result signifies only that the potential reckoned from the solution to mercury at the maximum is about ·04 volt less in the case of $n/10$ KOH

than in that of $n/10$ KCl. A result which, as before, is in agreement with the forms and relative positions of the electrocapillary curves.

The electrocapillary curves for the null solutions of KI and of KOH are shown in fig. 5.

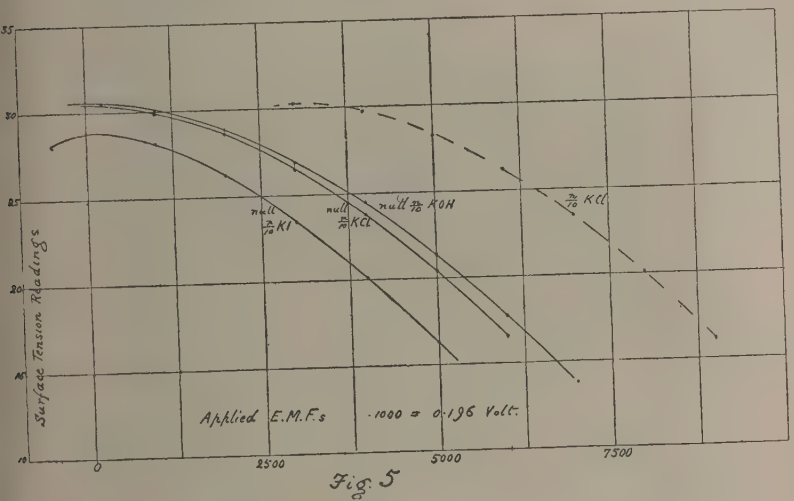


Fig. 5

The results of our experiments may be summarized as follows:—

§ 21. *Summary of Conclusions.*

1. The potential-differences between different null solutions and mercury are not the same. This is proved, allowing for the contact p.d. between electrolytes, by measuring each p.d. against the p.d. Hg | KCl, and also by measuring one null solution against another. The result is also deducible from the electrocapillary curves alone, without introduction of the question of the p.d. between electrolytes.

2. If the null-solution potential-differences are assumed to be zero, the values obtained for the p.d. Hg | $n/10$ KCl vary from about 0·53 volt to 0·79 volt. Assuming that the p.d. at the electrocapillary maximum is most likely to be zero when the maximum is undepressed, it is probable that the p.d. Hg | $n/10$ KCl does not exceed 0·53 volt.

3. The polarizing E.M.F. required to produce the maximum surface-tension between mercury and a given electrolyte has been proved by Paschen to be equal, in many cases, to the E.M.F. of the corresponding dropping-electrode circuit. This relation is shown to be true in four particular cases in which each E.M.F. is equal to zero. It is also shown that in none of these cases is the p.d. Hg | electrolyte necessarily zero.

4. It is shown that the Paschen relation immediately fails when the chemical action at the drop-electrode due to atmospheric oxygen becomes appreciable.

5. The Paschen E.M.F. between mercury and a solution of KCl remains unchanged on the addition to the solution of small quantities of Na_2S, although the natural p.d. between mercury and the KCl solution is thereby altered by more than half a volt.

6. A critical percentage of Na_2S was found for which the natural p.d. just mentioned altered with extreme rapidity, as in the cases studied by Behrend, in which he observed the variation of the E.M.F., Hg | $Hg_2(NO_3)_2$ | Hg, produced by the gradual addition of KCl or KBr at one electrode. In the present case the change in the p.d. Hg | electrolyte was deduced directly from the electrocapillary curves.

Discussion.

Mr S. Skinner congratulated the Authors upon the accurate series of experiments which they had carried out.

Dr W. Watson expressed his interest in the paper, referring especially to the action of dissolved oxygen present in the solutions.

Mr F. E. Smith referred to the fact that in the paper values for the contact p.d. were given to four places of decimals, and asked if any significance could be attached to the last two figures. He pointed out that the results obtained from drop electrodes were very different from those obtained by Billitzer using a different method. He asked if experiments had been made with jets of various sizes and under various pressures, and whether the form of the curves had been sufficiently studied.

Mr Lewis asked if the Authors had used other substances besides Na_2S, and if they had taken account of chemical actions which might take place at the electrodes.

Dr Erskine Murray referred to experiments he had made some years ago on contact potential-differences between metals in which the

oxygen of the air behaved in a manner analogous to the dissolved oxygen in the Authors' solutions.

Mr S. W. J. Smith, replying to Mr F. E. Smith, said that Palmaer's value for the contact potential-difference between mercury and $n/10$ KCl solution was quoted from his paper. With regard to Billitzer's views, they laboured for the present under the disadvantage that other observers had tried, but failed, to reproduce the effects which he describes. The form of the electrocapillary curve had been carefully studied. Van Laar had formulated a theory based upon the fact that the curve can be considered to consist within the limits of experimental error of portions of two parabolas. His interpretation of the significance of the point at which the curve changes from one parabola to the other had in reality no experimental support. The question of the character of the jet, amount of immersion, &c., had been carefully studied, and certain relations between the E.M.F. and the time of contact with the liquid had been arrived at. His (Mr Smith's) point of view differed from that of Paschen in that he believed the experimental evidence to show that the E.M.F. between a Paschen electrode and an electrolyte was not in general zero. He cited a case in which apparently the p. d. between a Paschen jet and one electrolyte ($ZnSO_4$) differs by nearly half a volt from that between a Paschen jet and another electrolyte ($CuSO_4$). It was only when the electrocapillary maxima for two electrolytes were equal that the Paschen E.M.F.s for the electrolytes were the same. An electrocapillary maximum could not be obtained for $CuSO_4$ solution, probably because of deposition of copper on the mercury, just as a maximum could not be obtained from concentrated H_2SO_4 on account of the evolution of hydrogen. Paschen's experiments did not prove that the p. d. between an electrolyte and a mercury-jet breaking in its surface is zero. It was possible that a certain fraction (in some cases the whole *e. g.* in null solutions) of the steady p. d. might arise practically instantaneously.

In reply to Mr Lewis, Mr Smith remarked that they used Na_2S because it was deducible from electromotive data—in agreement with chemical—that the solubility of mercury sulphide was extremely small even compared with that of calomel. In reference to Mr Lewis's suggestion that certain interactions might take place between the mercury, the dissolved salt and the Na_2S independently of the oxygen, he said that although he had found that the amount of Na_2S required (in the way the experiments were performed) was not chemically equivalent to the amount of oxygen in solution, yet the amounts of Na_2S and oxygen were found to be roughly proportional to one another in experiments they had performed with the help of Mr W. F. Higgins. He indicated to the meeting directions in which further experimental evidence was being sought. The electromotive method of tracing minute chemical change was both delicate and simple.

IX. *An Experimental Examination of Gibbs's Theory of Surface-Concentration, regarded as the basis of Adsorption, with an Application to the Theory of Dyeing.* (From the Muspratt Laboratory of Physical and Electrochemistry, University of Liverpool.) *By* W. C. M. Lewis, *M.A.**

Contents.

I. Object of the investigation; the characteristics of Adsorption Phenomena.
II. Theoretical Discussion; Gibbs's Theory of Surface Concentration; Milner's Calculations.
III. Experimental Methods and Apparatus; Results.
IV. Application to the Theory of Dyeing.
V. Summary.

I. Object of the Investigation.

Under the term "Adsorption" are grouped phenomena which may be regarded as forming an intermediate stage between chemical combination on the one band, and true absorption or solution on the other. Different types of Adsorption have been studied, but in general a solid substance (*e. g.* charcoal) has been utilized as the adsorbent body.

The present paper is an account of an experimental attempt at measuring adsorption effects quantitatively and interpreting the values obtained in the light of Gibbs's theory of surface-concentration. The treatment is novel in that the adsorption has been measured at a *liquid-liquid* interface; for it is only when dealing with liquid interfaces (or surfaces) that it is possible to measure interfacial- or surface-tension—a fundamental factor in the thermodynamic consideration of the question.

The Characteristics of Adsorption Phenomena.

The earlier investigations on adsorption dealt in general with the adsorption of gases on the surfaces of various solid materials. The case of vapours is of much more recent date, the most important instances being those of Travers† and

* Read February 28, 1908.

† Travers, Proc. Roy. Soc. series A, vol. lxxviii. p. 9 (1907).

Trouton *. Modern investigators have, however, dealt chiefly with the question of the adsorption of dissolved substances at the surface of some solid body in contact with the solution. Among the numerous recent memoirs on the subject may be mentioned those of Küster †, Schmidt ‡, Walker & Appleyard §, Biltz ‖, Lagergren ¶, and in particular Freundlich **. Freundlich's investigations contain the most systematic and accurate determinations yet recorded of the adsorption at a charcoal surface of a series of organic substances in aqueous solution. The general method was to prepare a solution of a certain substance (say a dye-stuff), and to a known volume of this solution to add a certain quantity of very finely powdered pure blood-charcoal. A certain amount of the dye is removed by the charcoal, the change in concentration being determined colorimetrically.

Among Freundlich's most important results may be mentioned that the equilibrium state is reached exceedingly rapidly—in about five seconds; that, using the same solid body the quantity adsorbed varies with the chemical constitution of the solute, *e.g.* aromatic acids are adsorbed in greater quantity than aliphatic; and finally, that the effects differed with the solvent used.

We may sum up the characteristics of adsorption which differentiate it from chemical combination thus:—

(1) The *order* in which a series of dissolved substances are adsorbed does not differ even when one substitutes as the adsorbing material, bodies as unlike as charcoal, silk, clay, and cotton. This is unlikely on the assumption of chemical combination.

(2) The reaction goes to an end almost instantaneously.

* Trouton, Proc. Roy Soc. series A, vol. lxxvii. p. 292 (1906).

† Küster, *Zeitschrift Phys. Chemie*, vol. xiii. p. 445 (1894).

‡ Schmidt, *Zeit. Phys. Chem.* vol. xv. p. 60 (1894).

§ Walker & Appleyard, Journ. Chem. Soc. vol. lxix. p. 1334 (1896).

‖ Biltz, *Ber. d. deut. chem. Gesell.* vol. xxxvii. p. 1706 (1904); vol. xxxviii. p. 2963 (1905).

¶ Lagergren, *Zeit. Phys. Chem.* vol. xxxii. p. 174 (1900).

** Freundlich, *Zeit. Phys. Chem.* vol. lvii. p. 385 (1906); vol. lix. p. 284 (1907).

(3) Heat effects, even in concentrated solutions, are undetectable. Chemical action, on the other hand, at relatively low temperatures is usually accompanied by evolution of heat.

Characteristics which distinguish Adsorption from Absorption.

The difference existing here (which has been attested by numerous determinations) may be stated thus: There is *not* a direct proportionality between the concentration of the solution or partial pressure of the solute and the amount adsorbed. To take an example from Walker and Appleyard's* paper on the adsorption of picric acid at the surface of silk.

The quantities of picric acid (remaining after the reaction, in the aqueous solution and in the silk itself are estimated) the following being the results obtained:—

TABLE I.

milligrams Picric Acid in 1 c.c. solution.	milligrams Picric Acid in 1 gram silk.	Ratio $\frac{a}{b}$
(a)	(b)	
0·064	13	0·005
1·98	37	0·053
7·0	75	0·094

Assuming the molecular weight of the picric acid to be the same in water and silk, the ratio $\frac{a}{b}$ should have been constant had true *absorption* taken place.

II. THEORETICAL DISCUSSION.

Gibbs's Theory of Surface Concentration.

A theoretical investigation of this subject from the standpoint of thermodynamics forms one of the chapters in Gibbs's† memoir on "Equilibrium in Heterogeneous Systems." He

* Walker & Appleyard, *loc. cit.*

† 'Scientific Papers of J. Willard Gibbs.' English edition, vol. i. p. 219.

first takes up the consideration of the mass or bulk equilibrium of a heterogeneous system, *i. e.* equilibrium in which any surface phenomenon is of insensible magnitude, and then proceeds to examine the case in which the surface area is relatively large and the influence of surfaces of discontinuity upon the equilibrium of heterogeneous masses becomes of importance. To use his own words :—

* "The solution of the problems which precede may be regarded as a first approximation in which the peculiar state of thermodynamic equilibrium about surfaces of discontinuity is neglected. To take account of the condition of things at these surfaces, the following method is employed :—

"Let us suppose that two homogeneous fluid masses are separated by a surface of discontinuity, *i. e.* by a very thin non-homogeneous film. Now we may imagine a state of things in which each of the homogeneous masses extends without variation of the densities of its several components, or of the densities of energy and entropy, quite up to a geometrical surface (to be called the dividing surface) at which the masses meet. We may suppose this surface to be sensibly coincident with the physical surface of discontinuity.

"Now if we compare the actual state of things with the supposed state, there will be in the former in the vicinity of the surface a certain (positive or negative) excess of energy, of entropy, and of each of the component substances. These quantities are denoted by ϵ^s, η^s, m_1^s, m_2^s, etc., and are treated as belonging to the surface. The ^{s} is simply used as a distinguishing mark, and must not be taken for an algebraic exponent.

"It is shown that the conditions of equilibrium already obtained relating to the temperature and the potentials of the homogeneous masses are not affected by the surfaces of discontinuity, and that the complete value of $\delta\epsilon^s$ is given by the equation

$$\delta\epsilon^s = t\delta\eta^s + \sigma ds + \mu_1\delta m_1^s + \mu_2\delta m_2^s + \text{etc.}$$

in which s denotes the area of the surface considered, t the

* Gibbs, 'Scientific Papers,' vol. i. p. 365.

temperature, μ_1 μ_2 etc. the potentials for the various components in the adjacent masses . . . . ."

"The quantity σ we may regard as defined by the [above] equation itself or by the following:

$$\epsilon^s = t\eta^s + \sigma s + \mu_1 m_1^s + \mu_2 m_2^s + \text{ etc.}$$

from which by differentiation and comparison with the former we obtain

$$d\sigma = -\eta_s dt - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_1 - \text{ etc.},$$

where η_s, Γ_1, Γ_2, etc. are written for

$$\frac{\eta^s}{s}, \quad \frac{m_1{}^s}{s}, \quad \frac{m_2{}^s}{s}, \text{ etc.},$$

and denote the superficial densities of entropy and of the various substances. We may regard σ as a function of t, μ_1, μ_2, etc., from which, if known, η_s, Γ_1, Γ_2, may be determined in terms of the same variables. An equation between σ, t, μ_1, μ_2, etc. may therefore be called a *fundamental equation for the surface of discontinuity*."

The final equation obtained above has been simplified and applied by Gibbs * to an actual case, viz.:—

"If liquid mercury meet the mixed vapors of water and mercury in a plane surface, and we use μ_1 and μ_2 to denote the [chemical] potentials of mercury and water respectively and place the dividing surface so that $\Gamma_1 = 0$, *i. e.*, so that the total quantity of mercury is the same as if the liquid mercury reached this surface on one side and the mercury vapor on the other, without change of density on either side, then $\Gamma_{2,1}$ will represent the amount of water in the vicinity of the surface *above that which there would be* if the water-vapor just reached the surface without change of density, and this quantity (which we may call the quantity condensed [*i. e.*, adsorbed] upon the mercury) will be determined by the equation

$$\Gamma_{2,1} = -\frac{d\sigma}{d\mu_2}.$$

In this equation and the following, the temperature is constant and the surface of discontinuity *plane*.

* Gibbs, 'Scientific Papers,' vol. i. p. 235.

" If the pressures in the mixed vapors conform to the law of Dalton, we shall have for constant temperature

$$dp_2 = cd\mu_2 ;$$

p_2 denotes the part of the pressure in the vapor due to the water-vapor, and c the density of the water-vapor. Hence

$$\Gamma_{2,1} = -c\frac{d\sigma}{dp_2} \quad \ldots\ldots "$$

Now applying the gas law $P = RTc$, finally we obtain

$$\Gamma_{2,1} = -\frac{c}{RT}\frac{d\sigma}{dc}.$$

This equation is of fundamental importance in that, if we assume its applicability to adsorption measurements, it contains the relationships between bulk-concentration, surface-tension, and quantity adsorbed in an experimentally determinable form.

The same expression may be obtained more simply as follows * :—

Consider the equilibrium at a surface (say of solid or liquid) in contact with a solution.

Let σ = surface-energy per unit of surface.

s = area of surface exposed to the solution.

m^s = the mass of solute adsorbed at the surface of the solid *in excess* of that normally present.

The temperature is supposed to be constant.

U = total energy of the heterogeneous film per unit of surface.

U can be increased :—

(1) by increasing the surface area, in which case the work required $= \sigma ds$;

(2) by increasing the concentration of the solute in the interfacial layer. This is proportional to dm^s namely μdm^s, where μ is the chemical potential of the solute.

Then $$dU = \sigma ds + \mu dm^s,$$

$$\therefore \quad d(U - \mu m^s) = \sigma ds - m^s d\mu.$$

* I am indebted to Prof. W. B. Morton for this deduction.

And since $d(U - \mu m^s)$ is a complete differential, we have

$$-\left(\frac{d\sigma}{d\mu}\right)_s = \left(\frac{dm^s}{ds}\right)_\mu,$$

but $\frac{dm^s}{ds}$ = mass adsorbed per unit area of surface, *i. e.* = Γ;

$$\therefore \quad \Gamma = -\frac{d\sigma}{d\mu}.$$

Now since

$$d\mu = RT\frac{dc}{c},$$

where c = the concentration of the solute in the bulk of the solution,

it follows that

$$\Gamma = -\frac{c}{RT}\frac{d\sigma}{dc}.$$

NOTE.—It should be noted that the expression obtained above occurs in Freundlich's paper already referred to. From the nature of his experiments it has been quite impossible to attempt a verification experimentally.

We have now to prepare a solution of certain strength c and measure the quantity adsorbed Γ as well as the value of $\frac{d\sigma}{dc}$. On substitution of the values in the equation we may obtain a verification or otherwise of the expression *. It may be stated at once that the results of experiments to be detailed do *not* show equality on the two sides of the equation—the discrepancy being always in the direction of Γ being many times greater than $\frac{c}{RT}\frac{d\sigma}{dc}$.

* While this work was in progress, the results of somewhat similar determinations were published by Milner (Phil. Mag. Jan. 1907 [6] vol. xiii. p. 96). These referred to equilibrium at the *air*-liquid surface. He has deduced an identical expression to that already given in this paper, and has applied it to acetic acid in aqueous solution and aqueous sodium oleate. He has found that the actual quantity removed from solution (Γ) is nearly ten times the calculated effect $\left(\frac{c}{RT}\frac{d\sigma}{dc}\right)$.

Reference might also be made to experiments by Zawidski (*Zeit. Phys. Chem.* xxxv. p. 77 (1900)) on the formation of the foam produced by the addition of saponine to aqueous solutions of hydrochloric and acetic acids. No measurements applicable to the present case were recorded.

III. Experimental Methods.

Use of a Liquid-liquid Interface.

As already stated, previous investigations with the exception of Milner's have dealt solely with adsorption at a solid surface—which does not allow of its surface-extent or surface-tension being determined. As it is necessary to evaluate these quantities, the possibility presented itself of measuring the adsorption of a solute at the interface between its solution and another liquid. This latter liquid must of course be absolutely chemically inert towards the solute itself and its solution. Choice fell on a hydrocarbon oil, since a body such as this is characterized by its chemical inertness. The next object was to obtain a substance, preferably soluble in water, which would possess the property of lowering the interfacial tension between water and oil. From their behaviour at the air-liquid interface it seemed likely that the soaps, saponine, and bile-salts would act in this way at the oil interface. The first experiments to be described were carried out with aqueous solutions of bile-salts.

In order to make certain that no chemical or solubility effects existed between the oil and the solutions, the following tests were carried out :—

(1) A portion of the oil was shaken up with water which was tested with phenolphthalein—neutral reaction, and therefore absence of free fatty acid as impurity.

(2) A portion of the oil was boiled for three hours with reflux condenser with $\frac{N}{10}$ methyl alcoholic potash—excess potash being titrated with standard acid. It was found that the acid required for neutralization was the same in amount as that for a blank experiment in which no oil was present. This proves the absence of fatty esters in the oil.

(3) Some of the bile-salt powder was shaken up with the oil, the latter allowed to stand, filtered, and a "drop-number" taken with the pipette (see later) against distilled water. The same drop-number was obtained as with the untreated oil fresh from the stock. Since the tension is a very delicate test for the presence of the salt, the above shows fairly

conclusively that there was no salt present in the oil after filtration, *i. e.*, the salt is insoluble in the oil.

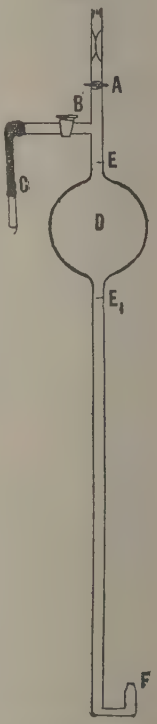
(4) The oil was shaken up with a solution of the salt, the oil filtered off and a drop-number taken against water. The same result exactly was obtained as with the oil which had been simply shaken up with distilled water filtered off and a similar drop number taken against water.

The above tests point conclusively to the fact that no effects of the nature of chemical combination or solubility take place between the oil and the bile-salt.

Examination of the Bile-salt.

A quantity of "sodium glycocholate" was obtained from Merck. On close examination, however, it appeared that this was far from pure. Besides sodium glycocholate there is also sodium taurocholate and other fatty acid alkali-salts. There were no inorganic substances such as sodium chloride or carbonate. Several determinations of the molecular weight (which is required, as will be seen later) by means of the lowering of freezing-point and rise of boiling-point of water gave as a result 140. Assuming complete dissociation in water, this would give the undissociated molecular weight 280. This latter was confirmed by a determination by the rise of boiling-point of alcohol, the result being 283. The osmotic molecular weight in water (viz. 140) is, however, the quantity required in the subsequent calculations.

Fig. 1.



Method of measuring the Interfacial Tension.

The Drop-Pipette method was employed, the apparatus being of the form shown in fig. 1. This was first filled with oil (by suction at C) up to the mark E. The tap B was then closed during a determination. The aperture F is carefully wiped before using, and the pipette placed in a fixed position relatively to the solution in all determinations.

The bulb D is of about 45 c.c. capacity between E and E_1. The distance E F is about 8 cms. As soon as the tall jar containing the solution is placed in position, tap A is turned full on, the constriction above only allowing very slow entrance of air; and hence the drops of oil rising through the denser solution are formed with exceeding slowness—at 12 to 15 secs. interval. This, as Lord Rayleigh * has pointed out, is of great importance in order to obtain fairly accurate determinations; the approximateness of the method being due to the application of a statical theory to what is really a dynamic phenomenon.

The method consisted simply in counting the number of drops formed while the oil fell from E to E_1.

Theory of the Drop-Pipette Method.

It may be used in the first instance simply to determine the *relative* tensions of solutions of different concentrations, thus:—

Let V = total volume of oil used,

n = total number of drops formed,

then the volume of each drop $= \frac{V}{n}$;

and if ρ = the density,

the weight of a drop $= \frac{V\rho}{n}$.

The tension σ is taken to be proportional to the weight of a drop,

$$\therefore \quad \sigma = K\frac{V\rho}{n}.$$

Similarly for another liquid,

$$\sigma_1 = K\frac{V\rho_1}{n_1}.$$

Hence

$$\frac{\sigma}{\sigma_1} = \frac{n_1\rho}{n\rho_1}.$$

As a result of the exhaustive work of Guye and Perrot †,

* Lord Rayleigh, Phil. Mag. [5] vol. xlviii. p. 321 (1899).

† Guye & Perrot, *Archives d. Sc. Phys.* 4th ser. vol. xi. p. 225 (1901); vol. xv. p. 132 (1903).

Kohlrausch *, and Lohnstein †, a determination of surface-tension in absolute measure by means of the drop-pipette can be obtained as follows :—

The expression giving the weight of a drop in terms of the tension is

$$g = r\alpha\Phi,$$

where α = tension in millgrms./mm.
g = weight of a drop in milligrams.
r = radius of the orifice in mms.
Φ is a function of $\left(\frac{r}{a}\right)$, where
a^2 is given by $\frac{2\alpha}{\rho}$,

ρ being the density of the liquid in the pipette.

This applies to cases of liquid-gas tension, but it may perhaps be extended to the present case by taking into consideration the density of the medium in which the drop of oil is formed, *i. e.* the water.

Calling the density of the water ρ_w, we have

$$a^2 = \frac{2\alpha}{\rho_w - \rho_0}.$$

We have now to evaluate Φ. The ordinary method of using the Lohnstein-Kohlrausch formula is to take some approximate value for α; from this calculate a, and hence $\left(\frac{r}{a}\right)$. Kohlrausch ‡ has given a table showing the values of Φ for different values of $\left(\frac{r}{a}\right)$ and by inter- or extrapolation Φ can be evaluated. We then compare the value of g given by the expression $r\alpha\Phi$ with g actually obtained by experiment; and finally, by a series of approximations, α is given such a value as to make the calculated and observed values of g identical.

Now a determination by Pockels § gives the value 48·3 dynes as the tension between water "and a petroleum oil."

* Kohlrausch, *Ann. d. Physik*, vol. xx. p. 798; vol. xxii. p. 191 (1906).

† Lohnstein, *Ann. d. Physik*, vol. xx. pp. 237, 606; vol. xxi. p. 1030 (1906).

‡ Kohlrausch, *loc. cit.* p. 805.

§ A. Pockels, Wied. *Ann.* lxvii. p. 668 (1899).

Assume in the present case

$$\alpha = 48 \text{ dynes per cm.}$$
$$= 4{\cdot}89 \text{ milligrams per mm.}$$

Then $a^2 = 97{\cdot}8$;

$\therefore\ a = 9{\cdot}8,$

$r = 1{\cdot}5.$

Hence $\left(\frac{r}{a}\right) = 0{\cdot}152.$

Unfortunately this value of $\left(\frac{r}{a}\right)$ is a little beyond the lower limit of Kohlrausch's table, viz. :—

$\frac{r}{a}$	Φ.
.....	.....
0·300	4·45
0·288	4·48
0·200	4·66

For $\left(\frac{r}{a}\right) = \cdot 152$, the value of Φ by inspection of these numbers (assuming the values do not change in direction down to $\left(\frac{r}{a}\right) = \cdot 152$) would be

$$\Phi = 4{\cdot}72;$$

hence $g = 34{\cdot}62$ milligrms.

Now g found experimentally $= 35{\cdot}00$ milligrms.

The value for the interfacial tension was therefore taken to be 48 dynes per cm. To distinguish this oil from another hydrocarbon oil which was found to have a tension of 33·6 dynes, they will be throughout designated oils "A" and "B," viz. :—

Interfacial tension { Water-oil A ..... 33·6 dynes per cm.
Water-oil B ..... 48 dynes per cm. *

* *Note.*—It may be as well to state here that although oil A was as carefully tested as oil B, the writer would lay greater stress on the accuracy of the determinations made with oil B.

Variation of the Interfacial Tension with the Concentration of Sodium Glycocholate Solutions.

First Series.—Oil A.

Aqueous solutions of the sodium glycocholate were prepared of the following concentrations:—

1 %, 0·8 %, 0·5 %, 0·33 %, 0·25 %, 0·18 %, 0·125 %, 0·1 %, 0·05 %, 0·01 %, 0 001 %.

On being freshly prepared, the aqueous solutions of these concentrations were quite transparent, but with considerable rapidity—2 to 3 hours—in the case of the more dilute, a white turbidity manifested itself. All tension measurements were therefore made with fresh transparent solutions so that the values obtained might be quite comparable.

The following table gives the results obtained with oil A. The first column gives the concentration of the solution; the second, the corresponding drop-number; the third gives the relative tension as deduced from the relation already obtained (pp. 159, 160), viz., that the drop-numbers are inversely as the tension; the fourth column gives the absolute values of the tension based on the oil-water determination 33 6 dynes/cm. and by applying the values of column 3.

Table II.—Oil A.

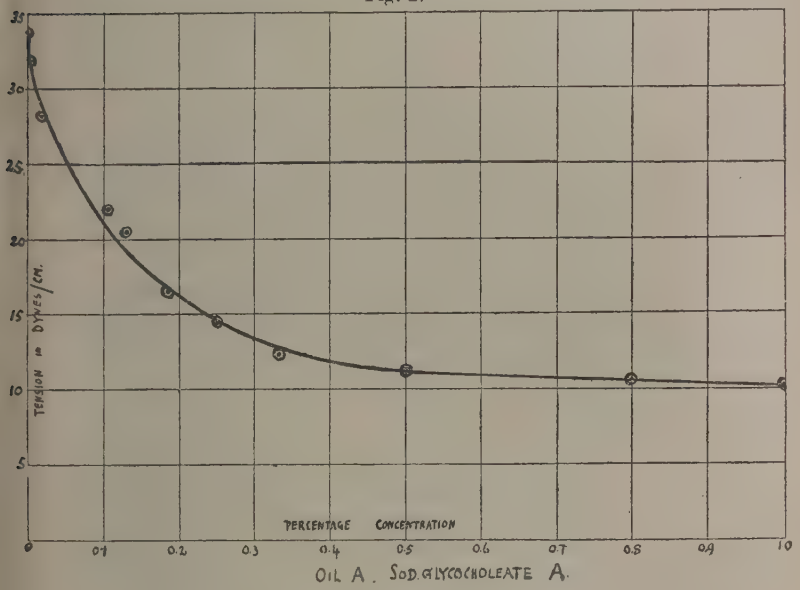
Per cent. Concentration.	Drop-number.	Relative Tension.	Tension dynes/cm.
0	183	1·000	33·60
0·001	191	0·958	32·20
0·01	219	0·836	18 08
0·05	244	0·750	25·21
0·1	280	0·654	21·96
0·125	297	0·616	20·70
0·18	365	0·501	16·81
0·25	418	0·438	14·71
0·33	489	0·374	12·57
0·5	536	0·341	11·48
0·8	558	0·328	11·03
1·0	566	0·323	10·86

The above values in columns one and four are plotted in fig. 2. It will be noticed how exceedingly marked is the lowering effect of the sodium glycocholate upon the interfacial tension.

We are therefore, now, in a position to obtain an experi-

mental value for $\frac{d\sigma}{dc}$ by simply taking the value of the tangent to the curve fig. 2 at the desired concentration.

Fig. 2.



SECOND SERIES.—OIL B.

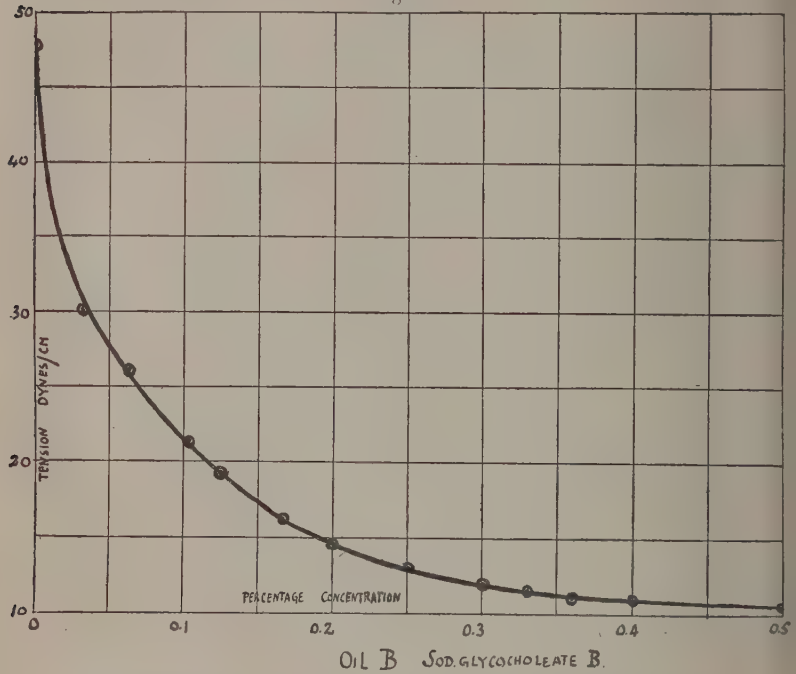
A similar series of determinations with oil B are given in the following table:—

TABLE III.—Oil B.

Per Cent. concentration.	Drop-number.	Relative Tension.	Tension dynes/cm.
0	128	1·000	48
0·0312	202	0·633	30·38
0·0625	233	0·549	26·35
0·125	317	0·404	19·39
0·165	375	0·341	16·37
0·200	417	0·307	14·73
0·250	471	0·272	13·05
0·300	522	0·245	11·76
0·330	531	0·241	11·57
0·360	557	0·230	11·04
0·400	568	0·225	10·80
0·500	585	0·219	10·51

The above absolute values of Tension and Concentration are plotted in fig. 3.

Fig. 3.



Oil B Sod. glycocholeate B.

In order to ascertain how far the values for the Tension obtained directly from the drop-number (column 4, Table III.) agreed with those obtained by applying Kohlrausch's formula

$$g = r\alpha\Phi$$

in each case, a comparison is made of the weights of the respective drops, using the values of the tensions for the two concentrations ·25 per cent. and ·5 per cent.

Per cent. Concentration.	Weight of drop $g=r\alpha\Phi$.	Weight of drop actually found.
zero, *i.e.* distilled water	34·62 milligrms.	35 milligrms.
·25 per cent.	8·89 „	8·60 „
·5 „	7·01 „	6·93 „

Having in the foregoing obtained data for the experimental determination of the coefficient $\frac{d\sigma}{dc}$ in the case of two different oils, the next procedure was to determine the value of Γ, *i. e.* the mass adsorbed per cm.^{2} of oil-surface in excess of that which would have been there had no adsorption taken place at all. To express this quantity Γ more briefly, the term "Adsorption Coefficient," following the nomenclature of Ostwald, has been employed.

Measurement of the Adsorption Coefficient.

Although the Adsorption Coefficient is defined as the excess mass of solute adsorbed, yet since the normal amount of solute per square cm. surface (when no adsorption has taken place) is very small in the present instance, this normal amount may be neglected in comparison to the total amount adsorbed per square cm. This is justifiable, as is evident from the following figures from an experiment detailed later:—

The bulk concentration of the glycocholate solution $=\cdot25$ per cent. or $\cdot0025$ grams per c.c.

Assuming the thickness of the surface layer to be of the order of the range of molecular attraction, namely, $13\cdot4\times10^{-6}$ cms. (according to Parks *), while the quantity adsorbed per cm.^{2} in this particular case is $5\cdot4\times10^{-6}$ gram, the layer evidently possesses a concentration of $\cdot403$ gram per c.c. The *surface* concentration is therefore about 160 times the *bulk* concentration.

It has been assumed that the thickness of the layer is of the dimensions of the range of molecular action. Of course the actual case is that there is a gradual "shading off" of the excess from the surface into the bulk of the solution, but *practically all* the excess is in the molecular surface-layer. This follows from the fact that the magnitude of the adsorption depends on the surface-tension, which is a phenomenon whose effects do not extend beyond the range of molecular attraction. As Gibbs † says:—"It is only within very small distances of such a surface that any mass is

* Parks, Phil. Mag. [6] vol. v. p. 517 (1903).

† Gibbs, 'Scientific Papers,' vol. i. p. 219.

sensibly affected by its vicinity—a natural consequence of the exceedingly small sphere of sensible molecular action."

The experimental determination of the adsorption coefficient of sod. glycocholate at the surface of a hydrocarbon oil was carried out, employing two distinct methods according as the adsorption took place under one of the two following conditions:—

(1) Adsorption at a very curved surface.
(2) Adsorption at an approximately plane surface.

(1) *Adsorption at a very curved surface.*

A certain volume of sod. glycocholate solution of known strength is shaken (by a motor-driven shaker) for several hours, with a known volume of oil so as to form a uniform emulsion. The bulk concentration of the solution after emulsification is estimated, and the fall in concentration gives the total quantity of glycocholate adsorbed. To measure the adsorbing area, the droplets of the emulsion are examined under a microscope having a scale of known value in the eyepiece, and the average diameter of a droplet taken. Hence we obtain the radius r and the volume of a droplet $=\frac{4}{3}\pi r^3$. Knowing the total volume of oil emulsified, we obtain the total number of droplets *, and since each drop has a surface area $4\pi r^2$, we finally obtain the total adsorbing area. Dividing the total quantity adsorbed by this area, the adsorption coefficient is determined.

The following are typical examples:—

Determination with Oil A.

One litre of sod. glycocholate solution approximately ·33 per cent. was made up, and of this 500 c.c. were shaken with ·447 c.c. oil for 12 hours and allowed to stand 18 hours. The volume of oil was obtained by weighings—the density of the oil being ·907. A drop of the emulsion was examined under the microscope.

* Assuming that the density of an oil-droplet in the emulsion will sensibly coincide with the density of the oil in bulk.

Average radius of a droplet $= \cdot 0000425$ cm.

Hence surface area of one droplet $= 4 \times 3 \cdot 1416 \times (\cdot 0000425)^2$.

and volume of one droplet $= \frac{4}{3} \times 3 \cdot 1416 \times (\cdot 0000425)^3$.

Total volume of oil emulsified $= \cdot 447$ c.c.

$\therefore$ Total number of drops formed $= 1 \cdot 3 \times 10^{12}$.

$\therefore$ Total adsorbing surface $= 31{,}553$ cm.^{2}

To estimate the quantity adsorbed :—

A drop-number was taken with the pipette through a portion of the original solution. Drop-number $= 483$, corresponding to a tension 12·80 dynes, which on fig. 2 indicates a concentration 0·318 per cent. After adsorption had occurred, a drop-number through the emulsion gave 459 corresponding to a tension 13·44 dynes, which again corresponds on fig. 2 to a concentration ·295 per cent.

$\therefore$ Fall in concentration $= \cdot 023$ per cent.

This was the general method adopted to determine change in concentration, it being much more delicate than any purely chemical means. It will be noticed that in the above the assumption is made that the emulsion particles themselves would not affect the value given by the pipette for the tension of the solution in which the emulsion is suspended. Justification of this is afforded by the concordance between the results obtained for the adsorption by this method and by an entirely different method to be described later. Continuing:—

Fall in concentration of ·023 per cent. $= \cdot 115$ gram for the 500 c.c. solution employed.

Hence the mass adsorbed per cm.^{2}, *i. e.*

$$\Gamma = \frac{\cdot 115}{31{,}553}$$

$$\Gamma = 3 \cdot 6 \times 10^{-6} \text{ gram.}$$

Similar determination of Γ, *using Oil B* :—

The solution made up gave a drop-number 531, corresponding on fig. 3 to concentration ·317 per cent. 250 c.c.

of solution were emulsified with ·160 c.c. oil (density ·900), and after emulsification the drop-number was 507, corresponding on fig. 3 to a concentration ·290 per cent.

Hence the fall in concentration .....=·027 p. cent.

∴ Total mass adsorbed from the 250 c.c. soln.=·067 gram.

Total adsorbing area .....=11058 cm.²

$$\therefore \Gamma = 5{\cdot}9 \times 10^{-6} \text{ gram per cm.}^2$$

A further determination with a solution whose original concentration was ·2 per cent. gave a value for the adsorption coefficient

$$\Gamma = 4{\cdot}7 \times 10^{-6} \text{ gram per cm.}^2$$

An estimation of the probable error of these values really depends on the estimation of the radius of the emulsion particle. As great care as possible was taken to obtain these very uniform in size. The radius of a drop is taken as being ·0000425 cm. The maximum value would be represented by

$$r = {\cdot}00005 \text{ cm.},$$

and as a minimum,

$$r = {\cdot}000035 \text{ cm.}$$

Substituting these values in the first determination with oil B, we obtain the following result:—

$r = {\cdot}000035$	cm.,	$\Gamma = 4{\cdot}4 \times 10^{-6}$	grm. per cm.²
$r = {\cdot}000050$	,,	$\Gamma = 6{\cdot}9 \times 10^{-6}$	,, ,,
$r = {\cdot}0000425$	,,	$\Gamma = 5{\cdot}9 \times 10^{-6}$	,, ,,

It is evident from these figures that the method is not sufficiently accurate to detect a different value of Γ corresponding to solutions of strengths ·317 and ·2 per cent. respectively. The different values obtained are within the limits of experimental error.

Comparison of Experimental values of Γ *with Calculated values.*

The calculated value for Γ is, as already pointed out,

$$-\frac{c}{RT}\frac{d\sigma}{dc}.$$

Let us take as a example the second determination with oil B :—

The concentration of the solution $= c = \cdot 2$ per cent.
$= \cdot 002$ grm. per c. c.

Temperature $T = 289$ abs.

R is the gas constant. For one gram of solute,

$$R = \frac{2 \times 4 \cdot 2 \times 10^7 \text{ ergs}}{\text{molecular weight}}.$$

The molecular weight determined as already described is 140 in aqueous solution.

The coefficient $\frac{d\sigma}{dc}$, read from the curve fig. 3 at the point where $c = 2$ per cent., gave

$$\frac{d\sigma}{dc} = \frac{9 \cdot 5 \text{ dynes}}{\cdot 002 \text{ grm. per c. c.}} = 4750.$$

The true value of this probably lies between the limits 4800–4700, *i. e.*, an error of about 2 per cent.

Hence

$$-\frac{c}{RT}\frac{d\sigma}{dc} = \frac{\cdot 002 \times 4750 \times 140}{2 \times 4 \cdot 2 \times 10^7 \times 289}$$

$$= \underline{5 \cdot 5 \times 10^{-8}} \text{ grm. per cm.}^2$$

$$\Gamma \text{ (found)} = \underline{4 \cdot 7 \times 10^{-6}} \text{ grm. per cm.}^2$$

That is to say, the actual quantity adsorbed is about 85 times the calculated amount. This is far beyond experimental error, and there can be no doubt that a real discrepancy does exist. To confirm this, however, a different method of experimentally determining Γ was resorted to in which emulsions were dispensed with, as it was thought possible that the radius of the drops might be too near the value for the range of molecular forces.

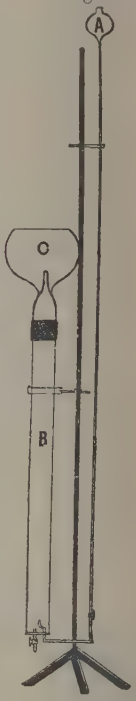
(2) *Adsorption at an approximately plane surface.*

In the previous emulsion method we have been dealing with tension and adsorption at very curved surfaces. Owing to the discrepancy obtained in the above method, it is

necessary to carry out determinations at a practically plane surface—*i. e.*, one of very small curvature in comparison with the curvature of the sphere of molecular action.

For this purpose the apparatus shown in fig. 4 was devised. It consists of a bulb A, of about 170 c. c. capacity, which is filled with oil. This bulb is connected to a long vertical narrow tube ($1\frac{1}{2}$ metres high), having a rubber joint and pinchcock near the base so as to regulate the flow of oil. The upwardly directed nozzle of this tube is inserted through a cork into a wider tube B (1 cm. radius), which contains the solution through which the oil rises in the form of large drops. The tube B becomes constricted near the top, and then opens into a large cup-like vessel C. The sod.-glycocholate solution (about 1 litre) is poured into B and C until the constricted end of B is about 3 cms. below the surface of the solution. The upwardly moving drops of oil adsorb on their surface some of the solute and carry it through the constriction, the drops eventually coalescing. The object of the constriction is to prevent the sod. glycocholate, which has once more been partially returned to solution (by the coalescence), from being carried back into the lower part of the tube. When A is empty, the tube B (which has a rubber joint near the top) is nipped at this point and the upper portion disconnected. The lower solution (which is 250 c.c. in volume) is run off from below, and a drop-number through it taken with the pipette. The fall in concentration is read off by means of fig. 3—or, rather, a somewhat enlarged form of fig. 3; the enlargement being necessary for accurate readings on account of the very small changes in concentration produced by this method, the fewer large drops offering a very much smaller surface than the emulsion particles.

Fig. 4.



Example: *Oil* B.

One litre of ·25 per cent. sod. glycocholate was prepared. The solution was poured into B and C as described, and after the drops have been passing for about 2 hours the reservoir A was empty and the contents of tube B run off. Through this solution a drop-number gave 466, *i. e.*, a tension of 13·2 dynes, corresponding on the curve to a concentration ·243 per cent.

Hence the fall in concentration = ·007 per cent.

∴ for 250 c.c. (the volume of B) the total quantity removed = ·0175 grm.

The volume of the oil-reservoir = 168 c.c.

The time of formation of 50 drops was taken at the beginning, in the middle, and near the end of the experiment. It was found that the middle value was the mean of the beginning and end, viz. 50 drops in 40 seconds.

Total time of emptying A . . = 7940 secs.
∴ total number of drops . . = 9925.
Hence volume of a drop . . = ·0169 c.c.
∴ radius of a drop . . . . = ·160 cm.
and hence total adsorbing area = 3192 cm.^{2}

∴ Adsorption coefficient = $5{\cdot}4 \times 10^{-6}$ gram per cm.^{2}

A second determination was made in which three times the former quantity of oil was used, and hence a greater fall in concentration was observed, which is in favour of a more trustworthy result :—

Total volume of oil used . . = 504 c.c.
Total time of dropping . . = 20520 secs.
Total adsorbing area . . . = 7414 cm.^{2}
Total mass adsorbed . . . = ·022 grm.

∴ Adsorption coefficient = $3{\cdot}1 \times 10^{-6}$.

It is worthy of note that these values are of quite the same order as those obtained at the very curved surface in the emulsion method.

The calculated amount for this particular concentration (0·25 per cent.) gave

$$\frac{c}{RT}\frac{d\sigma}{dc} = 3{\cdot}6 \times 10^{-8} \text{ gram per square cm.}$$

We therefore find in this case also, that the experimental value for Γ far exceeds the calculated value. Thus over 98 per cent. of the total observed effect is *un*accounted for in the theoretical calculation.

This result is unexpected, especially when one remembers that in this latter method of determining Γ the condition of planeness of surface is fulfilled to a very high degree of approximation; for the drops at the surface of which adsorption took place were of practically the same diameter as those produced by the drop-pipette in carrying out the measurements of $\frac{d\sigma}{dc}$; *i. e.*, the drops are very large in comparison to the sphere of molecular action. One would have expected, therefore, that the calculated result (dependent as it is on the value of $\frac{d\sigma}{dc}$) would be in good agreement with the experimental value of Γ.

One point of considerable interest lies, however, in the good agreement observable in the *experimental* values of Γ obtained by the two methods. On the one hand it appears to point (at least as far as one may rely on the accuracy of the determinations of Γ) to the fact that the tension even at very great curvatures does not differ appreciably from that at an approximately plane surface. On the other hand, since the portion of the adsorption which is unaccounted for is so much greater than the value required by theory, it is possible that even considerable variations in this latter would be undetected owing to the "swamping" effect of the excess values.

Discussion of Results.

The net result of the foregoing experiments is to show that between observed and calculated values there is a very great discrepancy—the actual quantity adsorbed being about eighty times the calculated amount. The most obvious explanation lies in the existence of some assumption in the theory which has been overlooked in practice.

The following are Gibbs's assumptions in the deduction of the equilibrium equation :—

(1) The adsorbing surface is plane.
(2) The solvent is to show no concentration at the interface.
(3) For the particular equation used in the present paper, there is supposed to be only one component capable of being adsorbed.
(4) This component and the solvent in which it is dissolved are supposed to form a single phase.

(1) *Planeness of the surface.*—It may be readily assumed that adsorption measurements made at the surfaces of oil-drops of sensible magnitude approximate exceedingly closely to those at a plane surface.

(2) *Absence of surface-concentration of the solvent.*—This was simply assumed to be the case, no means of testing its validity having as yet suggested itself.

(3) *Adsorption of a single component.*—This follows from the general experimental conditions, the solute, the sodium glycocholate, being the only substance whose adsorption is measured.

(4) *Adsorption from a monophase system.*—This assumption is implied from the actual example of surface-concentration given by Gibbs as exemplifying his theory, viz.:—A mixture of mercury- and water-vapours meeting at a liquid mercury surface, the water being the component which suffers surface-concentration. Mixtures of vapours are essentially monophase systems; and the question is, are we dealing with a monophase system in the case of an aqueous solution of sod. glycocholate? The evidence given by its osmotic behaviour in raising the boiling-points of water and alcohol and lowering the freezing-point of water, is strongly in favour of its being a true electrolyte, and hence of its solution being a monophase system.

Temperature Effects accompanying Adsorption.

All attempts at a direct determination of heat evolution or adsorption at the oil surface were negative. It may be shown, however, indirectly that a small *evolution* of heat must occur, from the observed variation of the interfacial tension with temperature. Thus, with a solution of concentration ·3 per cent. and oil B, the following results were obtained:—

Temperature.	Tension in dynes per cm.
16° C.	11·76
41° C.	12·96
67° C.	14·4

We have here the remarkable phenomenon of the tension *increasing* with the temperature. But in similar experiments, using water alone instead of solution, there was a marked fall in the tension, as was to be expected, viz.:—

Temperature.	Tension in dynes per cm.
16° C.	48
41° C.	40·8
67° C.	37·1

The increase in tension with temperature in the case of the glycocholate solution is to be accounted for, therefore, by partial "desorption" having taken place; that is, an increase of temperature in the case of the glycocholate solution decreases the quantity adsorbed, and hence, in accordance with the principle of Le Chatelier, adsorption must be accompanied by heat *evolution*.

Further experimental determination may make it possible to calculate the quantity of heat (Q) evolved per gram-mol. adsorbed by applying the equation

$$\frac{d \log K}{dt} = \frac{Q}{RT^2},$$

where K = ratio of concentration in surface layer to the bulk concentration.

IV. Application to the Theory of Dyeing.

The various theories which have been advanced to account for the process of dyeing may be roughly divided into

(1) Purely chemical combination or solid solution.
(2) Purely physical surface effects (*i. e.*, Adsorption).
(3) Partially surface effects and partially chemical combination.

A great mass of evidence has been brought forward in support of these different views, but it is not proposed in this place to discuss them *. Mention should be made, however,

* For an account of these various theories one may consult the work of W. P. Dreaper—'Chemistry and Physics of Dyeing' (1906).

of the most recent contribution, namely that of Freundlich *, whose results point very strongly to the absence of chemical combination, but leave it an open question as to whether dyeing is an example of adsorption in the sense of Gibbs's theory.

It is evidently essential to this view that dye-stuffs in solution should possess the property of lowering the interfacial tension. This, of course, cannot be determined in Freundlich's experiments owing to the presence of the solid phase, but considerable support would be given to the adsorption theory of dyeing if it were shown that dye solutions actually did lower the tension at the interface between the solution and an inert liquid. This liquid must of course be such as to exclude both chemical combination and solution.

With this object further measurements were made with the hydrocarbon oil B already experimented with, which was to function as the substance to be "dyed."

Aqueous solutions of various concentrations of the following dyes were prepared:—Congo red (sodium salt), methyl orange (sodium salt).

It is hardly to be expected that in any of these cases there would be solution in, or chemical combination with, the oil.

Congo Red.

A preliminary trial with this substance showed that there was a distinct lowering of interfacial tension. The following table gives the results obtained for solutions of different concentrations.

TABLE IV.

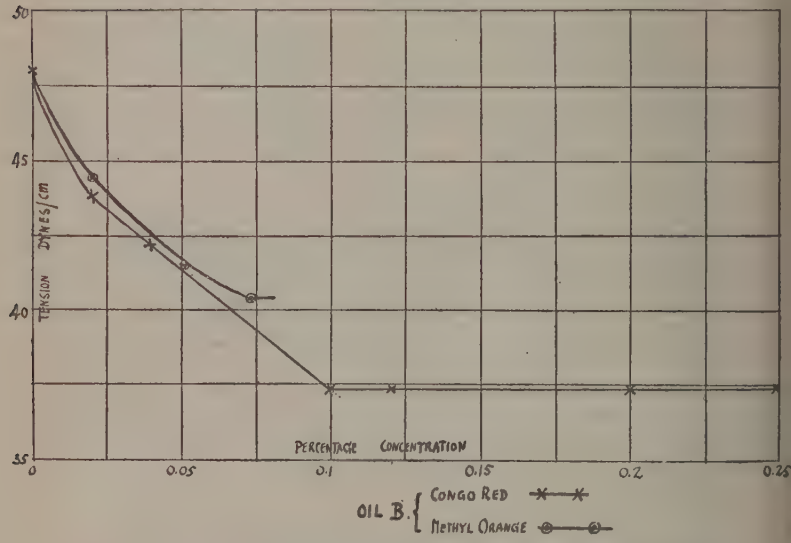
Per cent. Concentration.	Drop-number.	Relative Tension.	Tension in dynes/cm.
0·0	128	1·0	48
0·02	140	0·914	43·87
0·05	148	0·865	41·52
0·1	165	0·775	37·20
0·12	165	0·775	37·20
0·2	165	0·775	37·20
0·25	165	0·775	37·20

* Freundlich, *Zeitschr. Phys. Chem.* vol. lix. p. 284 (1907).

The results of Table IV. are plotted in fig. 5 (lower curve).

It will be noticed that after the concentration has reached 0·1 per cent. there is no further effect on the tension. This probably represents the maximum true solubility of the dye; and the minimum value for the tension might possibly be made use of as a practical method of ascertaining the optimum concentration for the dye-bath.

Fig. 5.



From the lower curve (fig. 5) we obtain the value of the coefficient $\frac{d\sigma}{dc}$, for the curve itself is practically a straight line. We may proceed, therefore, to apply the adsorption equation already obtained and calculate the adsorption coefficient (Γ).

Thus, taking as an example the solution of concentration 0·1 per cent.,

$$c = \cdot 001 \text{ grm. per c.c.},$$

$$\frac{d\sigma}{dc} = \frac{8 \text{ dynes}}{\cdot 001 \text{ grm./c.c.}}.$$

$$\therefore \frac{c}{RT}\frac{d\sigma}{dc} = \frac{\cdot 001 \times 8 \times 690}{289 \times 2 \times 4{\cdot}2 \times 10^7 \times \cdot 001} = \underline{2{\cdot}3 \times 10^{-7}} \text{ gram per cm.}^2$$

where 690 = the molecular weight of the undissociated Congo red, assuming it to be a monosodium derivative. Of course there is doubt as regards the value, since we are dealing with the substance when dissolved.

Thus, assuming complete dissociation in solution, the value of the molecular weight would be 345, and the resulting value for the adsorption coefficient would be $1{\cdot}15 \times 10^{-7}$ grm. per cm.^{2} On the other hand, if the dye is colloidal the molecular weight might possibly be much higher; though the behaviour of sod. glycocholate, by analogy, is rather against this.

Experimental result :—

250 c.c. of 0·1 per cent. Congo-red solution were shaken for fifteen hours with ·175 c.c. of oil. The resulting emulsion particles were examined under the microscope. It was found that $r = \cdot 0000435$ cm.

Hence, calculating exactly as in the sod. glycocholate solutions, we obtain the Total adsorbing area $= \frac{3 \times \cdot 175}{\cdot 0000435}$ cm.^{2}

The quantity adsorbed was determined as usual by taking a drop-number with the pipette through the emulsion. The drop-number was found to be 158, = that is, a tension 38·73 dynes/cm., corresponding on fig. 5 to the concentration ·082 per cent.

$\therefore$ Fall in concentration $= \cdot 045$ grm.

$\therefore$ Adsorption coefficient $\Gamma = \underline{3{\cdot}7 \times 10^{-6} \text{ grm. per cm.}^2}$

It will be observed that this is *very much the same value as was* obtained in the case of the sod. glycocholate, and shows a large discrepancy as regards the calculated value. The fact, however, of a lowered tension shows that adsorption effects in the sense of Gibbs's theory cannot be absent.

Methyl Orange.

The solubility of this substance in water is small—a saturated solution being about 0·073 per cent. The following results were obtained :—

TABLE V.

Per cent. Concentration.	Drop-number.	Relative Tension.	Tension in dynes/cm.
0	128	1·0	48
0·018	138	·927	44·49
0·036	143	·892	42·81
0·073	152	·842	40·41

These values are plotted in fig. 5 (upper curve).

It will be noted that fig. 5 has a marked difference in appearance to figs. 2 & 3. This is of course due to the solubility limit being reached in the former case before the tension has fallen much in value.

Experimental determination of Γ :—

250 c.c. of ·07 per cent. solution were shaken with oil and formed an emulsion.

The Fall in concentration = ·032 per cent.

$\therefore$ Total mass adsorbed = ·08 grm.

Adsorbing surface area $= \frac{3 \times \cdot 204}{\cdot 0000435}$ cm.^{2}

$$\therefore \Gamma = 5{\cdot}5 \times 10^{-6} \text{ grm. per cm.}^2$$

Calculated value $= 1{\cdot}2 \times 10^{-7}$ „ „

We have here a further repetition of the observed anomaly.

In considering the behaviour of these dyes in relation to the adsorption theory, it may be admitted that despite the discrepancy between the observed and calculated results, substantive dyeing, at any rate, must be more or less an adsorptive process. Possibly the actual mechanism of dyeing consists *first* in adsorption and *afterwards* coagulation possibly due to "colloidal neutralization." There may finally be some degree of chemical combination, which varies from case to case.

Note on Rosaniline hydrochloride and Crystal Violet.

A saturated aqueous solution of Rosaniline hydrochloride (about ·06 per cent.) gave a drop-number of 140—*i. e.*, a Tension of 43·87 dynes/cm. The decrease in interfacial tension is less marked than in methyl orange or Congo red. No further experiments were carried out with this substance. Also Crystal Violet dye concentration 1 per cent. gave a drop-number 230, and hence also shows a lowering of tension.

V. Summary.

1. The object of the investigation has been to examine from an experimental standpoint Gibbs's theory of surface-concentration, as the chief cause of the phenomenon of Adsorption. By modifying Gibbs's fundamental expression for surface-concentration, an equation is obtained giving the mass of solute adsorbed per cm.^{2} in terms of the concentration of the solution and the change in tension at the interface, aqueous solution—hydrocarbon oil.

2. The material employed consisted of aqueous solutions of bile-salts, the solute being adsorbed at the hydrocarbon-oil surface. The mass adsorbed per cm.^{2} oil surface was determined by two methods. The corresponding tension measurements were carried out by the drop-pipette method.

3. The results show a considerable discrepancy between the actual amount adsorbed and that calculated on Gibbs's theory—the actual amount measured being always in excess to the extent of twenty to eighty times the theoretical values.

4. Experiments with dye-stuffs show similar behaviour, the discrepancy being of the order stated.

5. As regards the discrepancy noted, no suggestion is as yet offered. Further experiments are in progress employing other electrolytes and non-electrolytes as material for measurements of a similar nature.

In conclusion, I would express my indebtedness to Professor Donnan for his advice and criticism during the course of this work.

Discussion.

Mr S. W. J. Smith remarked with reference to the Author's opinion that possible concentration changes at the surface of the mercury might have some bearing upon contact potentials, that Warburg had developed a theory of electrocapillarity based upon this assumption. It had been

shown that mercury drops falling through a solution of a salt produced changes of concentration, just as in the Author's experiments concentration changes were produced in a solution by rising drops of oil. There were at least two different interpretations of the mercury experiments.

Mr A. Campbell asked if the absorption of moisture from the air by cellulose was a case of adsorption, and also if the amount of adsorption in dyeing depended upon the temperature.

Mr Lewis said there was little doubt that the deposition of moisture on cellulose was a case of adsorption. Adsorption is accompanied by an evolution of heat, and a rise of temperature decreases adsorption.

X. *Observations on Recalescence Curves.* *By* Walter Rosenhain, *B.A., B.C.E., of the National Physical Laboratory.*

[Plate VI.]

The importance of the recalescence phenomena which occur in the cooling of steel and other alloys renders it desirable that the methods of observation used in the study of these phenomena, and the interpretations of the indications derived from these methods, should be fully discussed and understood. This is the more necessary since various workers have adopted different methods of observing recalescence phenomena, and hold somewhat divergent views as to the relative values of these methods. The author has therefore undertaken an investigation of two of these methods which, in various modifications, are widely used at the present time. This investigation has taken the form of a theoretical discussion of the physical facts which are represented by the cooling-curves obtained, and a consideration of the experimental means requisite for an approximate realization of the conditions indicated by the theoretical considerations. Examples of experimentally obtained cooling-curves are then given and discussed with a view to illustrating the possibilities of the various methods. Finally, an observation of a recalescence in crystalline silica, which was observed in the course of the experiments made in connexion with the present investigation, is described.

* Read January 24, 1908.

The two methods of obtaining cooling-curves, to which reference has already been made, may be called the "time-temperature" and the "differential" methods respectively. These names are justified by the fact that in the first class of measurements, observations of time and temperature are alone used for obtaining the data from which the cooling-curves are plotted; while in the second class time measurements are not employed, observations being made of the temperature of the body under experiment and, simultaneously, of the difference of temperature which exists between this body and a "blank" or neutral body cooling at approximately the same average rate. As will be seen below, the data obtained by each method may be represented graphically in several different ways.

For the study of all cooling phenomena, we may regard as fundamental the curve which is obtained when observations of time and temperature are plotted in a simple time-temperature curve, on which any given ordinate represents the temperature of the cooling body at the time corresponding with the abscissa. If the body in question

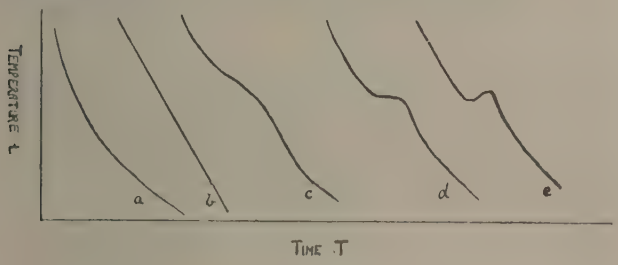


Fig. 1.

cools steadily, *i.e.* without undergoing any changes involving an evolution or absorption of heat or a change in specific heat, this curve will take a form somewhat like fig. 1 (*a*), where temperature (*t*) is plotted vertically and time (T) is plotted horizontally. The form of this curve will, of course, depend on the law of cooling followed by the body in question: for the case of a constant rate of cooling the curve will be a straight line, as in fig. 1 (*b*). If, during

the cooling process, the body undergoes a change involving an evolution of heat, the resulting curve on this diagram will take the form of fig. 1 (*c*), (*d*), or (*e*), according to the quantity of heat evolved and to the rate at which it is evolved. As there is a connexion between the shape of the curve and both the quantity of heat evolved and the rate of its evolution, it is interesting to enquire whether the form of the curve, or of a curve derivable from it, can be utilized to give quantitative data regarding the heat evolutions.

It is evident that at any point A of a time-temperature curve (fig. 2) the body under observation is losing heat at a definite rate. In the absence of any recalescence this rate of loss of heat would result in a rate of cooling indicated by a curve whose shape would be the same as that of the cooling-curve of a neutral body of the same thermal constants. At the moment of the beginning of recalescence (A) the body is losing heat at a rate proportional to the angle which the tangent to the cooling-curve at that point makes with the axis of time. In the case of a small evolution of heat, which does not produce a very large hump on the curve, it will not involve any very great error to suppose, first, that the rate of cooling of the ideal equivalent neutral body, cooling along the line of the dotted curve ABC, would have remained constant during the time occupied by the recalescence; and, secondly, that the actual body is losing heat at this same rate during the entire time of the recalescence. With these assumptions made, it follows that the quantity of heat generated is proportional to the greatest vertical distance between the two curves ABC and ARC, which is indicated by the line BR in the diagram. This line represents the greatest amount by which the temperature of the recalescent body exceeds that of an ideal equivalent neutral body. We may illustrate this from the special case where heat is added to a body which is not losing any appreciable amount of heat.

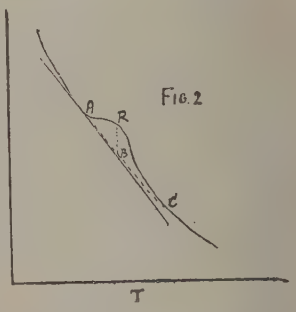


Fig. 2

In that case the curve ABC is a horizontal line, and the rise of temperature produced is proportional to the quantity of heat entering the body. In the case of a body losing heat at a *constant* rate, we may approximately write "excess of temperature" in place of "rise of temperature" in the adiabatic case.

In practice, however, two errors, corresponding to departures from the conditions assumed above, make themselves seriously felt. In the first place, if the recalescence extends over a considerable time, either because the quantity of heat evolved is very large, or because the evolution does not take place at one definite temperature but is spread over a considerable range, the rate of cooling can no longer be regarded as constant. This departure from the assumed conditions will result in making the line BR shorter than it should be if strictly in proportion to the quantity of heat evolved. Further, during the time that the recalescent body is passing along the portion of the curve from A to R its conditions of cooling, or rather the rate at which it is giving out heat, are not identical with its condition in this respect when at the point A. At the latter point the body is still cooling uniformly with its immediate environment, *i. e.* the furnace etc. in which it is contained, but as soon as the fall in the recalescing body is arrested, a difference of temperature is set up between the recalescing body and its environment which results in a loss of heat from the body at a greater rate than that denoted by the tangent to the curve at A. This also will result in shortening the line BR, more particularly in the case of rather rapid and vigorous evolutions of heat. It must, however, be borne in mind that a full discussion of the phenomena must also take into account the fact that the temperature of the furnace will also be affected by the more rapid transfer of heat from the recalescing body—a process which tends to lessen the amount of error introduced by the effect previously considered. All that we are therefore justified in concluding is, that there is a relation between the amount of heat generated and the length of the line BR, but that this relation only approaches proportionality under conditions of gradual cooling at a nearly constant rate and

for evolutions of heat which do not produce very large humps in the curve.

With the same degree of approximation just indicated for the proportionality between the quantity of heat evolved and the length of the line BR (*i.e.*, the vertical distance between the two time-temperature curves), the shape of the curves can also be used as a guide to the rate of evolution of heat, *i.e.* the intensity of the reaction producing the recalescence. At any instant up to the end of recalescence, the length of the line BR represents, approximately, the quantity of heat generated, and therefore the rate at which this length increases measures the rate of evolution of heat. If the curve ABC is approximately a straight line, the rate of increase of BR will be a maximum where the curve ARC approaches most nearly to the horizontal.

In practice it is not convenient to plot the observations of cooling, even when taken in the form of time and temperature measurements, in the form of a simple time-temperature curve such as we have so far discussed. The observations taken are generally those of the time intervals which elapse while the temperature of the body under observation falls through a definite small range. These intervals are then plotted as abscissæ with the temperature of the body as ordinate. In this way the well-known inverse-rate curves are obtained. It will be seen at once that this curve simply represents the differential coefficient with respect to temperature of the simple time-temperature curves which we have just discussed. In those curves time (T) was plotted against temperature (t), while in the inverse-rate curve the time dT, occupied by a fall of temperature (dt), *i.e.* $d\mathrm{T}/dt$, is plotted against temperature (t). The relationship between the two curves is now readily understood.

In fig. 3 let the line LMN represent an inverse-rate cooling curve. The area enclosed by an infinitesimal element of the curve and its abscissæ with the axis of t is given by $d\mathrm{T}/dt \,.\, dt$, and therefore the area included between the curve and the axis of t between values t_a and t_b of t is $\int_a^b d\mathrm{T}/dt$ and the value of the integral is $\mathrm{T}_b - \mathrm{T}_a$; *i.e.*, it represents the time

which has elapsed during the cooling of the body from the temperature t_a to the temperature t_b. Now, if we find the value of this time both for the recalescing body and for an ideal equivalent neutral body, and subtract one from the other, the difference represents the retardation in time which has resulted in the cooling of the body under observation in consequence of the evolution of heat. This retardation in time, multiplied by the rate of loss of heat from the body under observation during that time, measures the difference between the quantity of heat lost by this body and an ideal neutral body cooling at the same rate, and this excess of heat is obviously the quantity generated by the recalescence.

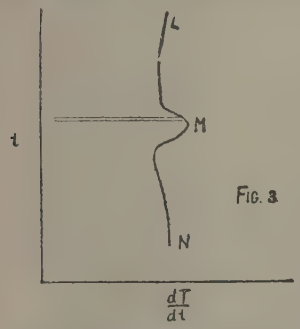


Fig. 3.

At first sight, therefore, such a curve appears to give much useful information; but the difficulty of knowing the rate of loss of heat of the recalescing body introduces exactly the same errors here as we have already considered in the case of the line BR (fig. 2), and a further difficulty remains to be considered. This arises when we have to decide between what limits the time, *i. e.*, the area of the curve in fig. 3, is to be taken. The correct limits are obviously the beginning and end of the recalescence; but while the beginning of the recalescence may be well marked, the end is not readily ascertained. Owing to the fact that during the recalescence the fall of temperature of the recalescing body lags behind that of the furnace, as soon as the recalescence has ceased, the body under observation for a time undergoes much more rapid cooling, ultimately—more or less according to circumstances—completely recovering its equilibrium with the furnace in which it is contained. The result is, on the time-temperature curve, a steep portion following the flattening due to the recalescence, while the inverse-rate curve approaches considerably nearer to the zero than does the curve of an ideal neutral body. From the present point of view it follows that if the time T in the inverse-rate curve

be taken over too wide a range, the acceleration of cooling just described will materially affect the result: indeed, this is almost obvious when we consider that the total time occupied by the cooling of a small specimen of steel, for example, contained in a fairly large furnace is not very much affected by the small amount of heat generated by the recalescence of the steel. The choice of the limits between which the value of T shall be taken on the curve in fig. 3, therefore, becomes of serious importance. It will not be correct to take the point where the time-temperature curve of the recalescing body becomes parallel to that of the ideal neutral body as indicating the end of the recalescence. The recalescing body is losing heat rather faster than the neutral body would do at the same instant, so that when the rate of fall of temperature in the hotter body becomes the same as the rate of fall in the colder (neutral) would be, there must still be an evolution of heat making good the difference in the rates of loss of heat. The end of the recalescence therefore lies just beyond the point where the actual observed curve and the ideal blank become parallel. In the inverse-rate curves this is represented by a point just beyond that at which the observed curve crosses the ideal blank. It is from the beginning of the recalescence up to this point that the time (T) must be measured by means of the area of the peak of the inverse-rate curve if a value proportional to the amount of heat generated, divided by the mean rate of loss of heat from the body during recalescence, is to be obtained. We have already indicated that this cannot be done with any degree of certainty. All that can be said of the inverse-rate curve therefore, is that, provided the rate of cooling be the same in the two cases, a peak of larger area on such a curve, indicates the evolution of a greater quantity of heat, but this comparison cannot be relied upon to any degree of accuracy unless the general shape of the two peaks to be compared is similar. Where recalescences extend over long ranges of temperature, the quantitative indications of these curves are very vague indeed. Perhaps the most important case in which the comparison of the areas of several peaks would be of interest, if they could be correctly interpreted

in terms of heat evolution, is that of a single cooling-curve showing several recalescences at various temperatures, such as are met with in the cooling of mild steel. Here the difficulty arises that the rate of cooling when the body is at a temperature near 800° C. is different from that when the same body is near 700° C.; and, unfortunately, the change in the rate of cooling of an actual blank body such as a piece of platinum or of asbestos, cannot be applied directly to the case of the recalescing body, for the reasons already indicated. In cases of this kind, the state of affairs is further complicated by the fact that frequently a second recalescence commences long before the end of the rapid cooling which follows the cessation of the previous recalescence, with the result that—roughly speaking—a fresh hump is superimposed on the backward-sloping portion of the time-temperature curve. In such cases it is evident that the conditions are too complicated to allow of any quantitative evaluation of the phenomena, and the indications of the curves can be regarded as qualitative only.

As regards the intensity of a recalescence, *i. e.* the rate of evolution of heat, we have seen above that this is represented by the rate of change of the vertical distance between the observed and the ideal blank time-temperature curves—this representation being understood with the same limitations that apply to the other indications of these curves. This rate of change of vertical distance is simply equal to the difference between the slopes of the two curves. Assuming that the slope of the ideal curve is constant during the recalescence, this difference becomes inversely proportional to the slope of the observed time-temperature curve. But the slope of the observed curve is the rate of cooling of the observed body, and its inverse is the "inverse rate" ($d\mathrm{T}/dt$), which is plotted in the inverse-rate curves under discussion. We thus see that—to a rough degree of approximation—the height of the apex of the peak of an inverse-rate curve is proportional to the intensity of the heat evolution producing the recalescence, and its position on the temperature-scale indicates the temperature at which the reaction proceeds most vigorously. Here also the limitations that attach to the estimation of the quantity of heat evolved apply with

full force, so that it is only under special conditions that any quantitative value can be attached to the height of a peak. As a rule nothing more can be said than this, that under reasonably similar conditions of cooling a tall peak represents a rapid and a flat peak a gradual evolution of heat.

We turn now to a consideration of the differential method of obtaining cooling-curves. As already indicated, this method is independent of time measurements; what is actually determined is the difference in temperature between the body under observation and a blank or neutral body cooling at approximately the same rate, the observations of this difference of temperature being plotted as abscissæ against the actual temperature of the body under observation as ordinate. In the ideal case, which although not realizable in practice we may use as the basis of our discussion, the blank body is supposed to cool at the same rate as the recalescing body would have done in the absence of recalescences, and the time-temperature curves of the two bodies would then be represented by the two curves ABC and ARC in fig. 2. In that case, the observed differences of temperature would simply represent directly the values of a succession of vertical lines such as BR. In that case, the interpretation of the differential curve would be very simple, since—again with the limitations previously insisted upon—the maximum value of BR is proportional to the quantity of heat evolved, while the rate of evolution of heat is proportional to the rate of change of BR. In the ideal differential curve, therefore, the maximum height of the peak representing a recalescence would be proportional to the quantity of heat evolved, while the maximum rate of change of angle of the curve would measure the rate of evolution of heat during the change. The actual form of such an ideal differential curve is indicated in fig. 4, where, in the absence of recalescences, the curve is vertical. This condition is, however, not attainable in practice, since it involves the necessity for a similarity of properties as regards specific heat, thermal conductivity, &c. between the neutral or blank body and the body under observation. A case which is obtainable in practice is illustrated diagrammatically in fig. 5. Here,

quite apart from the occurrence of recalescences, there is a steady divergence between the time-temperature curves representing the cooling of the blank body and the observed body respectively, with the result that the differential curve shows a steady slope in one direction upon which the peak due to recalescence is superposed.

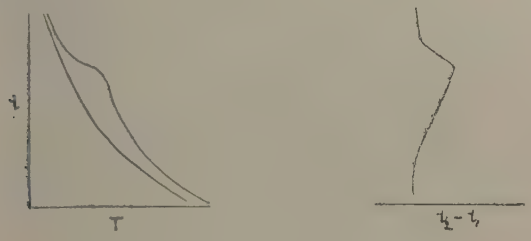


FIG 4

Provided that the slope of the differential curve is not too great, *i. e.* provided that the blank body does not cool much more rapidly or much more slowly than the body under observation, recalescences superposed on such a slope appear

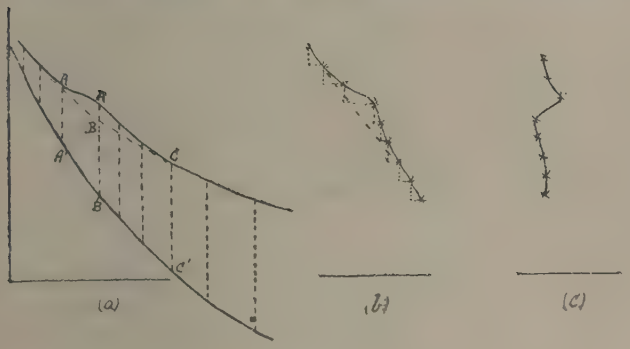


FIG. 5.

as perfectly definite peaks and are capable of the same interpretation as before. In fig. 5 (*a*), using the same notation as in fig. 2, we find that the abscissæ of the differential curve represent the lengths AA′, BB′, CC′, &c. If the recalescence

does not extend over a very great range of temperature, and if the divergence between the curves ABC and A′B′C′ is not very great, then we may take AA′=BB′=CC′, and the height of the peak of the differential curve still represents the length BR+ a quantity which is simply the average difference between the temperatures of the two bodies at the beginning of the recalescence. Even if the rate of divergence between the temperatures of the two bodies is considerable, we can arrive at an approximate estimate of the value of this average from the general slope of the differential curve. Graphically this is equivalent to drawing an assumed blank as indicated by the dotted lines in fig. 5 (*b*), and measuring the height of the peak of the differential curve from this assumed line. The error involved in making such a correction is in most cases smaller than the inaccuracy which, as we have seen, our ignorance of the exact cooling process renders unavoidable in connexion with the quantitative interpretation of all forms of cooling-curve.

In practice, particularly where rapid cooling is employed, it is sometimes found that the general slope of the differential curve becomes excessive, thus rendering the detection of the beginnings of small peaks difficult and uncertain; sometimes, indeed, this difficulty is felt in reading the indications of differential curves even when the general slope is not excessive. This difficulty will be readily understood when it is realized that fundamentally the differential curve is merely a reproduction on a somewhat different scale and on another base-line of the time-temperature curve. Therefore, just as it is found convenient in practice to plot the inverse-rate curve rather than the time-temperature curve, so it occurred to the author that the use of the "Derived Differential" curve *," in which the differential coefficient of the ordinary differential curve should be plotted, might prove more intelligible than the first differential curve itself (fig. 5 *c*). The examples shown in the second part of this paper have justified this supposition, and it therefore becomes desirable

* The curves referred to in this paper as "differential" cooling-curves would perhaps be more correctly described as "difference" curves, but since the method of obtaining these curves is widely known as the "differential method," it was thought desirable to retain the term.

to consider the exact interpretation of these "derived differential" curves.

Returning to the fundamental time-temperature curves of the two bodies, we may write the equations of their cooling-curves as follows:—$t_1 = f(T)$ and $t_2 = F(T)$, where $f(T)$ and $F(T)$ are two different but unknown functions of T, except that in the case of a constant rate of cooling $f(T)$, which represents the cooling-curve of the neutral body, takes the simple form $t_1 = kT$ where k is constant. The abscissæ of the ordinary or "first" differential curve are the values of $t_2 - t_1$ for various values of T, and we have

$$t_2 - t_1 = F(T) - f(T);$$

calling this R, we have

$$\frac{dR}{dt_2} = 1 - f'(T)\frac{dT}{dt_2},$$

where $f'(T)$ is the differential of $f(T)$ with respect to T.

Now dR/dt_2 is the quantity that is plotted as abscissa in the derived differential curve. It is interesting to note that, for a constant rate of cooling, for which $f'(T)$ becomes either unity or a constant, the quantity dR/dt_2, plotted against t in the derived differential, becomes a linear function of the quantity dT/dt_2, which is the quantity plotted in the inverse-rate curve (see above).

We thus see that under the only conditions which render the curves interpretable at all, the derived differential and the inverse-rate curves take exactly the same form and are capable of exactly the same interpretation. Where the rate of cooling is not constant, the curves will be somewhat different, but qualitatively their indications must be identical, and—so far as they are capable of quantitative interpretation at all—this must be applicable to both with the same degree of accuracy. The essential difference between the two systems of measurement and representation, lies in the fact that the retarding effect of recalescences upon the cooling of a hot body is measured and represented in one case as a retardation in time, and in the other case as a retardation in temperature. In the time method the rate of cooling is measured against an assumed uniform rate of

cooling, while in the differential method the temperature is measured against an actually uniformly falling temperature. Since time and temperatures are dependent variables whose relation over short ranges of temperature at all events does not differ widely from a linear one, it is only natural that the curves obtained by the two methods, if properly compared, should yield identical results.

Returning for a moment to the derived differential curve, we find for the area of a peak the value $\int \frac{dR}{dt_2} dt_2$, and this is equal to R between the limits of the beginning and end of the recalescence. R, as we have seen, measures the quantity of heat evolved, so that, with the same limitations as already indicated for the inverse-rate curves, the area of a peak on the derived differential curve is also proportional to the heat evolved by the recalescence. The rate of cooling is supposed known and taken into account in both cases, since this factor affects both the maximum temperature difference attained and the time of retardation to the same extent. Further, in the same way as it was shown for the inverse-rate curve, the area in question must be measured to that point of the curve representing the end of the recalescence, and this is equally difficult to ascertain in both curves.

From a fairly full consideration of the physical facts which determine the shape of cooling-curves as found by either the time or the differential method, we are led inevitably to the conclusion that as far as either qualitative or quantitative interpretation, and in fact as far as the detailed form of the curves is concerned, there is no distinction between the inverse-rate and the derived differential curves, both proving equally valuable as qualitative guides to the existence of recalescence, but both proving equally vague as far as quantitative results are concerned, except under very special conditions which are not readily realized in practice. The answer to the further obvious question as to which of the two methods is preferable in practice, must depend upon experimental considerations alone. These considerations are next to be discussed.

The experimental conditions to be realized in taking time-

temperature observations for the purpose of drawing inverse-rate curves are very simple in character. An accurate means of measuring the temperature of the body under observation and of recording the times occupied by small decrements of temperature, are all the appliances required; but these must be made of sufficient delicacy and accuracy to detect very small retardations in the cooling-process. On the other hand, the cooling-process itself must be conducted with perfect steadiness, *i. e.* the rate of cooling, apart from recalescences, must be perfectly steady and regular and remain unaffected by external circumstances. Unfortunately in practice these two conditions are difficult to reconcile, since it is found that when sufficiently delicate means of registering time and temperature are employed, slight irregularities in the rate of cooling become apparent even in the case of a body free from recalescences. This in fact constitutes the most serious disadvantage of the time-temperature method, since variations in external conditions translate themselves directly to the resulting cooling-curve. Where it is desired to accurately locate small evolutions of heat, it therefore becomes necessary to repeat the series of observations several times; and this is not only laborious, but is in some cases open to the objection that repeated heating and cooling, even *in vacuo*, affects the constitution of metals, particularly of those in which meta-stable equilibria are met with.

As regards the degree of sensitiveness required in the time and temperature measurements for the observations by this method in order to arrive at a degree of sensitiveness similar to that attainable by the use of the differential method, we may consider a case of cooling under typical conditions. If we consider a body cooling at the rate of say one degree Centigrade in 12 seconds, *i. e.* at a rate of about 300° C. per hour, which is a reasonably slow rate, small recalescences are frequently met with which cause a prolongation of the time required for a fall of temperature of 1° C. from 12 seconds to 20 seconds at the maximum. Taking a case of this kind, we have the following comparison:—

Temperature.		Time of falling. 1° C.	Difference of temperature on differential scale *.
From 651° C.		(say)	10·0° C.
650	to	12″	10·4
649		18″	10·9
648		20″	11·2
647		16″	10·8
646		8″	10·5
645		10″	10·4
644		12″	10·3

If we plot the derived differential curve and the inverse-rate curve from these observations, we may find that they are—as we should expect—very similar in character (see fig. 6). The effect of errors of observation on the two curves will, however, be very different. In the case of the time observations, an error of 0°·1 C. in the estimation of

Fig. 6.

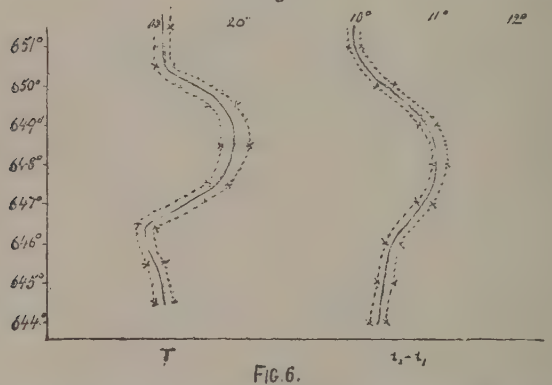


FIG. 6.

the temperature would result in an error in the observed time of one-tenth of the total interval, and larger errors in the temperature measurement will result in proportionately larger variations in the observed time intervals. In the case of the differential readings, a similar statement applies—

* The differences of temperature given in column III. are such as would correspond to the time observations of column II., assuming a constant rate of loss of heat. The calculations have been made by drawing the curves on a large scale and assuming an initial difference of 10° C. between the bodies.

an error of 0°·1 in the estimation of the temperature difference between the two bodies will affect the readings for the derived differential curve to the extent of from 10 to 20 per cent. The extreme variations in the two curves resulting from absolute errors of 0°·1 C. in the observations are shown by the crosses on the two sides of the two curves. With observations taken on instruments whose limit of accuracy in both cases is represented by 0°·1 C., the observed curves would show irregularities lying within the two dotted curves in each case, and in both cases these irregularities would not suffice to mask even the small recalescence here considered.

The actual temperature of the cooling-body in the case of the inverse-rate observations, as also the difference of temperature between the two bodies in the differential method, is very frequently measured by the deflexion of a sensitive galvanometer. Assuming that the scale is divided in millimetres and that the position of the moving spot of light can be read at any instant accurately to one-fourth of a scale-division, then to attain the degree of accuracy referred to above, it becomes necessary that the sensitiveness of the galvanometer, scale-distance, &c., shall be so arranged that in both cases 0°·1 C. is represented by a deflexion of not less than 0·25 millimetre. Now in the case of the direct-reading inverse-rate method, the same galvanometer is required to indicate temperatures of some 800° C., and with the above requirement to be satisfied this would demand a scale length of about 2 metres. The galvanometer of the differential apparatus, on the other hand, is only required to indicate differences of temperature which rarely exceed 40° C., and for this purpose a scale-length of only 100 millimetres would be required under the same conditions as were assumed for the direct method. While the latter condition is obviously quite easily fulfilled by a simple deflexion instrument, the requirement of adequate sensitiveness for the direct method cannot be met by a simple deflexion method even on the ground of length of scale alone. In fact, the only manner in which the direct or inverse-rate method can be rendered as sensitive as the differential method, is by the use of a potentiometer method in which the E.M.F. of the couple is partly balanced by that of a constant (standard)

cell and the deflexions used only over very short ranges of temperature. When this is done, the spot of light from the galvanometer moves across the scale as the temperature falls, but the entire scale only represents some 10° C.; and when a deflexion of that amount has been obtained, the spot of light is brought back to the opposite end of the scale by altering the variable resistance of the potentiometer, whereby the opposing E.M.F. from the standard cell is altered. This sensitive method has been adopted for the preparation of all the inverse-rate curves shown in the latter part of this paper. This method, however, exhibits certain very decided disadvantages. In the first place, the zero position of the galvanometer must be accurately known if time observations are to be made at more than one point of the scale, otherwise alternately long and short intervals will be systematically obtained. Unfortunately, the extremely delicate galvanometers required to give the requisite sensitiveness are very liable to zero creep, so that towards the end of long curves, some such regular alternations are nearly always to be found. Further, this sensitive method is unsuited to rapid cooling, since in that case the time taken for the galvanometer to become steady after the insertion of the plug in the potentiometer circuit is too long compared with the time-interval to be measured, and the next observing point is liable to be crossed while the galvanometer is still oscillating. From all these disadvantages the differential method is entirely free, for although a sensitive galvanometer is still required to give the differential reading, it is used over only a relatively short length of scale, and a slight amount of zero-creep does not affect the shape of the derived differential-curve materially. The practical consequence of this difference between the two methods is that while all "inverse-rate" curves show quite notable irregularities due to observational error, the readings of the differential method usually yield smooth and regular curves which require no smoothing. Since, at all events in the ordinary less sensitive forms of inverse-rate determinations, the experimental irregularities are frequently comparable in size with the peaks due to the smaller recalescences, it follows that these irregularities must be eliminated by repetitions of the same cooling-curve.

A serious drawback to both these methods of taking cooling-curves is the very laborious character of the observations. The inverse-rate method is, in this respect, more troublesome than the differential, for in the latter the observer has merely to record the deflexions of one galvanometer at the moment when another galvanometer shows a certain deflexion, and the differences between these successive observations are plotted directly as the "derived differential" curve. In the case of the inverse-rate method, on the other hand, the time observations, for accurate work, must be made by means of a chronograph indicating seconds, and before the curve can be plotted, many yards of tape must be counted in order to obtain the actual values of the observed intervals.

From this point of view, as also from that of obtaining objective evidence of the actual nature of the observed cooling-curves, the desirability of autographic means of obtaining these curves becomes evident. Apart from the use of the Schneider-Carpentier induction-galvanometer, which cannot be made adequately sensitive except for very rapid cooling, the only means of autographically recording the observations of the direct method lies in obtaining simple time-temperature curves, from which the inverse-rate curve would have to be obtained by graphic differentiation *. The fact that adequate sensitiveness involves the use of a very long scale, makes it impossible to carry this out in practice for accurate work. In the case of the differential method, the method devised by M. Saladin of causing the motion of one galvanometer to displace the beam of light in a vertical direction while the movement of a second galvanometer moves the beam horizontally, renders the production of autographic curves of adequate accuracy at all events possible.

* When the inverse-rate curve is plotted from time observations at finite intervals of temperature, the resulting curve may depart considerably from its true form. Thus for a strictly horizontal part of the time-temperature curve, $dt/d\mathrm{T}$ is zero and therefore dt (which is the abscissa of the inverse-rate curve) is infinite. If the time-temperature curve actually rises at any point of a recalescence, the inverse-rate curve should pass through infinity and reappear on the negative side. These considerations show the necessity of taking the inverse-rate observations at very short intervals of temperature in order to obtain close approximation to the true curve.

Referring to the quantitative comparison of the two methods given above, we see that with a given size of paper in an autographic recorder of any kind, the differential method is capable of from 10 to 20 times the sensitiveness of the direct method. At the present time, the only consideration adverse to the complete adoption of autographic apparatus for the determination of differential cooling-curves lies in the risk of error from zero-creep of the galvanometer. In the Saladin apparatus, one galvanometer gives the actual temperature of the body under observation, and the other galvanometer the differential reading corresponding to that temperature. A slight amount of creep in the latter instrument would not materially affect the result, but even a small amount of creep in the former instrument would vitiate the result by causing an error—not in the amount or magnitude of the recalescence—but in the temperature at which it would be indicated as taking place *. With ordinary moving-coil galvanometers the errors from this cause—with sensitive recording paper of moderate size—might amount to from 5° to 10° C., and this is too large an error to be admissible. By the use of a special galvanometer, having a bi-filar suspension which is entirely free from zero-creep, it is hoped to overcome this source of error and then to effect much saving of time and labour by the use of an autographic apparatus for obtaining differential curves. The possibility of doing this without sacrifice of the necessary sensitiveness is an advantage of the differential method which must not be underrated †.

In comparing the direct and differential methods of obtaining recalescence curves, several other experimental questions remain to be considered. In the first place, there is a very

* Zero-creep is, perhaps, responsible for some peculiarities of certain cooling-curves taken with the Saladin apparatus, which have been published. Thus Dr. Guillet was led to suppose that certain recalescences in copper-aluminium alloys took place at higher temperatures on cooling than the corresponding absorptions of heat on heating. A displacement of the zero of the temperature-galvanometer would account for this anomaly.

† The curves obtained by the Saladin apparatus are, of course, first differential curves, and would require conversion into the derived differential curves by graphic differentiation.

considerable difference between the two methods in respect of their sensitiveness to external disturbing causes. Serious external changes of temperature are, of course, liable to affect both methods, since the change in the rate of cooling may easily affect one of the two bodies in the differential method somewhat more rapidly than the other. On the other hand, smaller disturbances, such as are almost inevitable in most laboratories, are liable and in fact do affect the readings of the direct method while they leave the differential curve unaffected, since the difference in their effect upon the two cooling bodies is too minute to be traced upon the curve. From the point of view of the experimental refinements required, this is a great advantage in favour of the differential method.

An objection sometimes taken to the differential method arises from the fact that it involves the use of a neutral or "blank" cooling body, which is generally a cylinder of platinum. In order to approximate to the ideal condition of equal rates of cooling of the two bodies in the differential method, it would be desirable to use as the neutral body a substance having physical constants as nearly like those of the body under observation as possible. Owing, however, to the necessity of avoiding substances possessing recalescences of their own, the choice in this respect is very limited. In practice, platinum is found to have such different constants from those of iron and steel at all events, that the departure from ideal conditions is very marked, although it has already been indicated, and will be further proved by examples from actual curves, that the use of the derived differential curve eliminates the uncertainties thus introduced into the results. With a view to entirely avoiding the use of a neutral body in the differential method, the author proposed to apply the differential apparatus to the case of two pieces of the same material, cooling at approximately the same rate, but one somewhat retarded in time (and temperature) relatively to the other. This is readily accomplished by placing the two bodies in parts of the furnace which attain slightly different temperatures. One specimen of the material under observation will then commence its cooling from a somewhat lower temperature, and

will therefore arrive at a recalescence point before the other; the result will be a deflexion of the differential galvanometer in the direction indicating that the temperatures of the two specimens are approaching one another. As both temperatures continue to fall, the recalescence will be completed in the first body and will then begin in the second body, with the result that the deflexion of the differential galvanometer will be rapidly reversed, since while one body will temporarily remain at a stationary temperature, the other will be cooling particularly rapidly. Each arrest-point in the cooling-curve thus taken will therefore be represented by a double swing of the differential galvanometer. An actual curve of this kind is shown (fig. 12, Pl. VI.), but the usefulness of the method is, unfortunately, greatly impaired by the fact that in metals where several recalescences follow somewhat closely upon one another, their effects become superposed and the indications become confused and useless. From the point of view of the theory of cooling-curves, however, the method and example given in fig. 12 are instructive.

With regard to the general experimental details, such as the manner of inserting the thermo-electric junctions into the specimens, the arrangement of the specimen in the furnace and its protection, when required, from oxidation or other chemical actions, it need only be remarked here that the same precautions are required for both methods of determining cooling-curves.

In order to test by actual results the correctness of the reasoning outlined above, a number of experiments were carried out for the purpose of illustrating the capacity of the differential method of taking recalescence curves. The first of these consisted in taking a series of "blank" curves, the two cooling bodies being in some cases identical and of materials supposed to be free from recalescences of any kind. In the first experiment, the two thermo-junctions connected to the terminals of the differential galvanometer were simply placed centrally within the hot tube of an electric furnace, which was then heated to a temperature of about 1100° C., this temperature being measured by means of a third thermocouple attached to a delicate potentiometer. The resulting curve, in which deflexions of the differential galvanometer are plotted against

readings of the actual temperature of the furnace, is given in fig. 7 (*a*), Pl. VI. As would be expected under these circumstances, the curve is very nearly a vertical straight line ; it must be pointed out, in view of observations to be described below, that such a result can only be obtained if the furnace itself is of suitable construction, for while *small* irregularities in the cooling of the furnace are obliterated by the fact that they affect both differential couples in the same way and at the same time, this ceases to be true if there are any *large* irregularities in the cooling of the furnace, since if these should affect one of the couples before the other they would produce irregularities on the differential curve.

In the second experiment, two similar platinum cylinders were cooled together, one of the cylinders, however, being some 10 per cent. heavier than the other. As a result, the upper part of the differential curve (fig. 7 *b*) shows a slight slope which, however, dies away for the lower portions, where the cooling is more gradual. This is an example of a marked characteristic of the curves obtained by the differential method; *i. e.*, that they are more nearly vertical, and therefore depart less from the ideal conditions of equal cooling of both bodies when the cooling is gradual than when it is rapid.

In the third experiment, a cylinder of platinum was cooled against one of fire-clay in order to show the effect of very wide differences in the physical constants of the two bodies. As would be anticipated, the curve (fig. 7 *c*) shows a decided slope, the cooling of the fire-clay lagging considerably behind that of the platinum, but the curve is nevertheless satisfactory as a blank because it is quite free from irregularities, and a "derived differential" curve (fig. 7 *d*) derived from it in the manner indicated above is perfectly free from peaks. It should perhaps be noted that it would be quite possible so to arrange matters as to overcome the obliquity of the first differential curve in such a case by placing the cylinder which normally tends to cool more slowly in a part of the furnace which cools rather more rapidly ; but this would involve several experiments before the best position could be found and would therefore be too laborious, while the device of using the derived differential curve makes a general slope of the ordinary differential curve a matter of indifference.

In the following figures differential cooling-curves of some carbon-steels are given, the ordinary and derived differential curve being given in each case.

Fig. 8 (Pl. VI.) shows the differential and derived differential curves for a steel containing approximately 0·20 per cent. of carbon, the usual impurities being present in very small amounts only. This steel was kindly supplied to the Laboratory by Professor J. O. Arnold of Sheffield, for the purpose of comparing the results obtained in taking cooling-curves of this steel at the Laboratory of the Sheffield University with those obtained in the present experiments. Other cooling-curves of the same steel are given in figs. 13, 14, and 15 A described below. In fig. 8 it will be seen at once that the derived differential curve is far more definite in its indications than the first differential curve. This curve as well as the others given of this steel very closely resemble the curves obtained by Professor Arnold except that a doubling of the highest recalescence-point is described by Professor Arnold, but its existence is not shown in the present curve. In figs. 9, 10, and 11 similar first and derived differential cooling-curves are given for a series of very pure carbon-steels of increasing carbon content (0·326, 0·991, and 1·263 per cent. respectively). These steels were supplied to the Laboratory through the kindness of Mr. J. E. Stead, F.R.S., and although originally intended for another purpose, they have proved very useful for the present series of experiments. These curves, and particularly the derived differential curves, very clearly indicate the recalescence-points which are well known to occur in steels of this composition. In reading these curves, the temperature at which any given recalescence is to be regarded as taking place is that at which the point or apex of the peak of the derived differential curve is found to lie, since this is the temperature at which the most rapid evolution of heat occurs. If we compare the curves here given with those described in the paper by Carpenter and Keeling on "The Range of Solidification and the Critical Ranges of Iron-Carbon Alloys," * it will be found that the observed differential curves themselves are in most cases in very close agreement, but the interpretation adopted by the

* Journal of the Iron and Steel Institute, 1903, i.

authors of that paper differs somewhat from that which the present author deduces from the considerations here advanced. Messrs. Carpenter and Keeling appear to regard the temperature at which the apex of the differential curve is found as the "critical point"—in so far as they admit the existence of such "points" as distinct from ranges at all—while it now appears more correct to interpret the apex of the *derived* differential curve in this sense. There can, of course, be no doubt that in many of the transformations found in these and other alloys, the change occurs gradually and not entirely at one temperature; but for the purpose of arriving at an approximately correct equilibrium diagram, the author considers that the "points" as indicated by the apices of the derived differential curves should be used.

In order to further illustrate the use of the "derived differential" curve, differential cooling-curves were taken of specimens of one particular variety of steel under conditions of more rapid cooling than that adopted in the ordinary course. The author is inclined to regard a rate of cooling in which the temperature of the steel specimen falls from about 1000° C. to the ordinary temperature in the course of two hours as more or less "normal," since this rate of cooling appears to be slow enough to allow most of the transformations to take place completely, at all events in the case of the softer steels. Rates of cooling considerably more rapid than this are used by some workers, but since the object is to determine the *equilibrium* conditions, any discrepancies that arise between rapid and slow cooling must be interpreted in favour of the slower cooling method, since while too rapid a rate of cooling can, and often does, result in the partial suppression or displacement of thermal transformations, leaving the metal temporarily or permanently in a meta-stable state, too slow a rate of cooling cannot result in anything beyond the complete attainment of equilibrium conditions. It is therefore especially interesting to compare the curves shown in figs. 13 and 14 with those of fig. 8. These all refer to the cooling of samples of the same steel, but while in the case of fig. 8 the time occupied by the cooling process was about $1\frac{3}{4}$ hours, in the experiments represented by the curves of fig. 13 the apparatus was arranged to allow of more rapid cooling, and

the time occupied was accordingly only 35 minutes, while in the case of fig. 14 the cooling was arranged to take place almost in the free air and therefore only occupied about 12 minutes. It will be seen at once, on comparing these three figures, that the ordinary differential curves of figs. 13 and 14 are not at all readily interpreted by themselves, since the rapid cooling has resulted in a wide departure from the ideal conditions of equal cooling of the two bodies in the differential apparatus, the resulting first differential curves being extreme cases of the type illustrated in fig. 5. The derived differential curves of both 13 and 14 are, however, perfectly clear and readily interpreted, and they will be found, on comparison, to be in striking agreement both with one another and with fig. 8. The only discrepancy appears in the fact that there seems to be a difference in the relative intensities of the three transformations as shown by these three curves; as the relative size of the peaks on these curves is, however, considerably dependent on the rate of cooling in each case, the comparison of the three curves from this point of view cannot carry much weight.

For the purpose of comparison, cooling-curves of some of the same steels were also taken by means of the "inverse-rate" method, this method being applied by means of the very sensitive potentiometer installed at the Laboratory. In this instrument a fall in the temperature of the cooling body through 12° C. causes the spot of light on the galvanometer-scale to traverse 104 scale-divisions of 2 mm. each. At the end of this swing, the spot is brought back to the left-hand end of the scale by moving a plug on the resistance-box, and the galvanometer is sufficiently dead-beat for all oscillations to have died out long before the spot of light crosses the centre of the scale. Observations are taken every time the spot of light crosses the centre of the scale and also when a deflexion of 52 divisions is indicated, these points representing successive decrements of 200 micro-volts in the E.M.F. of the thermo-couple. The time observations are made by depressing a key which makes a mark on a chronograph-tape, accurate seconds being marked on the same by means of a relay actuated by the standard clock of the Laboratory; the resulting curves are shown in fig. 15, A & B, which should

be compared with figs. 8 and 9. The rate of cooling adopted for this method was the same as that used for obtaining the ordinary differential curves; and a comparison of the two sets of curves will show that their results are in substantial agreement, except that the "inverse-rate" method produces curves which suffer from much greater irregularities due to experimental imperfections than do the differential curves: this is undoubtedly due to the fact that in the case of direct time-temperature observations every external irregularity is translated to the resulting curve, and the more faithfully, the greater the sensitiveness of the apparatus employed.

The general conclusion which is, in the author's opinion, to be drawn from the results is that for most purposes the differential method of obtaining cooling-curves is eminently satisfactory; it has the advantage of being largely independent of external conditions and of the physical constants of the body under observation, and it has been shown to be applicable over a wide range of rates of cooling. The observations themselves are easily made and are not liable to any serious error, given reasonable care and skill on the part of the observer. The most serious criticism that could, perhaps, have been advanced against the method was the difficulty of correctly interpreting the curves in cases where the two bodies cooled at somewhat different rates; but the theoretical considerations laid down in the earlier part of the present paper, and the use of the derived differential curves here advocated, entirely remove that difficulty. On the other hand, while it is certainly possible to obtain "inverse-rate" curves showing all the small recalescences indicated by the differential method, this can only be done by using great experimental refinement, a very open temperature-scale, and moderate rates of cooling, and under these circumstances the method becomes very laborious and also subject to error from external disturbing causes.

For the purpose of the experiments made for the purpose of the foregoing investigation, some observations were made which not only are of interest in connexion with the experimental arrangements of cooling-curve apparatus, but are of some intrinsic importance, and are therefore to be described here.

The earlier "blank" curves taken with either bare thermo-junctions or two platinum cylinders, were obtained in an electric resistance-furnace of a type that has been introduced and described by Dr. H. C. H. Carpenter; this furnace consists essentially of a porcelain tube (of a material made for this purpose by Messrs. MacIntyre, of Burslem) wound with nickel wire and embedded in a thick lagging of finely powdered quartz. The blank curves thus obtained all showed, more or less clearly marked, a recalescence-point at a temperature of 580° C., and it proved a matter of considerable difficulty to trace the source of this evolution of heat. The platinum cylinders, the thermo-junctions themselves, and the nickel-wire winding of the furnace were suspected in turn, but each of these was found to be free from the actual recalescence. Finally, it was found that by using two bare couples and placing one close against the wall of the furnace-tube and the other well in the middle of the tube, a greatly increased recalescence could be detected. The curve obtained is shown in fig. 16 *a*. As it had already been shown that nickel showed no recalescence at this low temperature, the material of the tube itself was suspected, and a similar experiment was tried in an electric-resistance furnace by Heraeus, in which the platinum-resistance foil is wound on a tube of special Berlin porcelain; in this furnace the mysterious recalescence at 580° C. disappeared entirely. Messrs. MacIntyre then kindly furnished the author with some small cylinders of their porcelain, and these, cooled against a platinum cylinder in the Heraeus furnace, showed the recalescence clearly (see curve, fig. 16 *c*), but not so vigorously as would be expected if the whole mass of the cylinder were taking part in the reaction. The author therefore ascribed the recalescence to one constituent of the porcelain, and this view was confirmed when chemical analysis showed that the English porcelain contains a considerable proportion of free silica, whilst the special Berlin porcelain contains an excess of alumina. Differential cooling-curves of various kinds of silica were then taken (figs. 17 and 18) and in crystalline varieties, such as sand and quartz, very vigorous recalescences were obtained, but fused (vitrified) silica and precipitated silica were found to be entirely free from the reaction. The author accordingly

ascribes the recalescence found at 580° C. to a polymorphic change in crystalline silica, the occurrence of the recalescence being in fact a very sensitive test for the presence of free silica in ceramic materials. As to the nature of the change which silica undergoes at this temperature, both on heating and cooling, the author is unable to offer any suggestion; but it is interesting to note that in their recent paper on the Silica-Lime series, Messrs. Shepherd and Day * describe a polymorphic transformation in Silica (Quartz = Trydimite) as occurring at a temperature of 750°–800° C. The author's curves show no trace of any evolution of heat at that temperature, while the recalescence at 580° is so marked and constant both on heating and cooling, that there can be no doubt as to its occurrence at that temperature.

In another connexion, Le Chatelier and others † have noticed that in the heating of fire-clays and other similar bodies there are marked retardations at or near 600° C. The authors quoted have ascribed these retardations to one or more steps of the dehydration process; but there can be little doubt that one at least of these phenomena must be ascribed to the same cause as the recalescence in the author's curves of silica, viz., a polymorphic change in crystalline silica itself.

The same phenomena appear also to have affected the observations of Roberts-Austen, of Carpenter and Keeling, and of others on the lower recalescence-points of iron and steel. In the well-known differential cooling-curve of electro-deposited iron published by Roberts-Austen ‡ and throughout the diagram of the Iron-Carbon alloys as given by Carpenter and Keeling §, recalescence-points are indicated at or very near the temperature of 580° C.; and there can, therefore, be very little doubt that this recalescence is due to some silica contained in the walls or lagging of the furnaces used by those workers, and that therefore this point must be deleted from the Iron-Carbon diagram.

* Shepherd and Day, Amer. Journ. Science, October 1906.

† Le Chatelier, *Comptes Rendus*, tome civ. pp. 1443–1446, 1517–1520 (1887); W. C. Hancock, Journ. Soc. Chem. Ind., 1906.

‡ W. C. Roberts-Austen, "Fifth Report to the Alloys Research Committee," Proc. Inst. Mech. Engineers, 1899.

§ Carpenter and Keeling, Journ. Iron & Steel Inst., 1903, i.

The experimental portions of the above research were carried out in the metallurgical laboratories of the National Physical Laboratory, the author having been assisted, in the earlier portions of the work, by Mr. C. A. Edwards. The author also wishes to express his indebtedness to Mr. F. J. Selby, M.A., for help in connexion with the mathematics of this paper, and to the Director, Dr. R. T. Glazebrook, F.R.S., not only for the warm interest he has taken in the progress of the work, but also for valuable suggestions in reference to the theory of cooling-curves as discussed in the earlier part of this paper.

Discussion.

Mr F. J. Selby remarked on the skill with which the Author, by direct reasoning from certain approximate assumptions, had arrived at his interesting results as to the points of importance in connexion with recalescence curves. Mr Rosenhain had shown, very clearly and graphically, that from the theoretical point of view all the methods of representing the cooling-curves must give identical information, and that therefore the decision as to method to be adopted depended simply on the experimental accuracy attainable; while, in this respect, he had brought forward very strong evidence in favour of the Roberts-Austen differential method. Mr Selby suggested that it might be worth while to draw out theoretical cooling-curves based on certain simple assumptions as to the conditions of cooling. He showed how this might be done for the parts of the curve preceding and following the recalescence; and that by making a suitable supposition as to the variation in the rate of evolution of heat during the recalescence, such as $\frac{dQ}{dT} = (a-bT)^2 e^{cT}$, a complete theoretical curve might be drawn by the comparison of which with the experimental curve the constants might be determined and all the quantities of importance in connexion with the recalescence estimated with greater accuracy. In particular, and without any assumption as to the form of $\frac{dQ}{dT}$, some of the results in the paper could be verified; it could be shown that the evolution of heat was not completed at the peak on the derived differential curve (the point of inflection on the Roberts-Austen Curve), and the point of maximum evolution of heat on the experimental curve could be fixed. The value of the derived differential curve advocated by the Author becomes apparent from such calculations.

Mr A. Campbell remarked that the end of the paper was the part which would most likely be of interest to physicists. It was most interesting to find that the Author has shown (by the cooling-curve method) a change-point in silica near 580° C. Quite a number of years ago Le Chatelier showed that between 460° and 500° C. the coefficient of

expansion of quartz showed a quick increase, and he predicted that a change-point should occur at 270° C. Randall's experiments in 1905 on quartz showed a similar result so far as the expansion is concerned. Experiments which he (Mr Campbell) had made with nickel showed no abnormality in coefficient of expansion at temperatures which gave strongly marked thermo-electric change-points. For the direct reading of rates of cooling, Dejean not long ago devised an ingenious arrangement in which the thermocouple is connected to one coil of a differential moving-coil galvanometer whose other coil is connected to a second galvanometer: the readings of the latter will be a function of the rate of cooling. It occurred to the speaker that a transformer would give a simpler method of obtaining di/dt, but the slowness of change of i makes it too insensitive. The assumptions made in the paper that the specific heat, the thermal conductivity, and the emissivity of any material remain approximately constant even over a small range of temperature near recalescence, seem somewhat uncertain to the physicist, and must be regarded merely as working conventions by the metallurgist.

Mr S. W. J. Smith expressed his interest, from the consideration of magnetic data, in the Author's opinion that there is no critical point near 580° C. in the cooling-curves of iron and steel. It was curious that in the paper in which Roberts-Austen describes the critical point found at about 580° C., he cites the magnetic experiments of Morris in support of the fact that a change occurs in iron at that temperature. Morris puts the temperature of the magnetic change at about 550° in one specimen, but at about 500° in another; while in a third the effect was scarcely observable. Even in the specimen most studied, the magnitude of the effect seemed to depend upon the annealing temperature. In some experiments on permeability-temperature variation in nearly pure iron (·06 % C., ·1 % Mn) annealed at about 850° C., Mr Satterly and the speaker found a distinct change in the slope of the μ-θ curve (H=0·43) slightly below 500° during cooling, and a distinct minimum value of μ near 250° during heating. But with the field-strength used there was no apparent break in the slope of the μ-θ curve near 580° C. There was thus apparently no conclusive evidence from magnetic data of a critical point at 580° C. The effect observed at 580° by Roberts-Austen was very feeble compared with another effect which began near 500° and continued over a considerable range. This effect was obvious as a more or less pronounced "hump," of which the maximum lies near 400° on practically all the permeability-curves. It was even traceable in the curves of Hopkinson, although his observations below 500° were very few in number. Their own magnetic experiments agreed with those of Morris and with the Roberts-Austen cooling-curve in showing another critical point near 250°, although in their case the effect was only detected during heating.

XI. *The Distribution in Electric Fields of the Active Deposits of Radium, Thorium, and Actinium.* *By* SIDNEY RUSS, *Demonstrator of Physics, Victoria University, Manchester* *.

Introduction.

THE distribution in an electric field of the excited activity produced by thorium and radium emanations has been studied by several observers. Working with thorium emanation, Rutherford † has shown that the amount of activity imparted to a rod charged negatively decreases as the pressure in the containing vessel is reduced after a certain pressure is reached; while experiments made by Makower ‡ show that similar effects are obtained with the excited activity produced from radium emanation. Some further experiments by Rutherford § with the emanation from radium indicate that while at atmospheric pressure the greater part of the excited activity is directed to a cathode by moderate electric fields, yet a small fraction (about 5 per cent.) goes to an anode. Reasons are then (*loc. cit.*) given for supposing that some of the active deposit particles carry a negative charge, thus accounting for their transmission to the anode.

It seemed of interest then to find out whether the quantity of active deposit that goes to an anode changes when the pressure is varied.

A comparison has therefore been made over a range of pressure extending from ·001 cm. to 10 cms. between the amount of activity imparted to a rod charged positively and then negatively when exposed for the same interval of time to equal quantities of the radium emanation.

It was found that whereas the activity of the cathode decreased as the pressure was diminished, the anode showed a corresponding increase in activity.

The rod which had served as cathode or anode was then made a neutral pole by connecting it to the containing vessel,

* Read March 13, 1908.

† Rutherford, Phil. Mag. Feb. 1900.

‡ Makower, Phil. Mag. Nov. 1905.

§ Rutherford, Phil. Mag. Jan. 1903.

and what may be called diffusion experiments, *i. e.* with no electric field existing in the gas, were then made. Observations showed that there was a marked decrease in the amount of active deposit that diffused on to the rod as the pressure was diminished.

After a slight modification of the apparatus, a comparison of the activity obtained on a cathode and anode over a range of pressure extending from ·1 mm. to 1 mm. was made with three gases having widely different densities, namely, hydrogen, air, and sulphur dioxide.

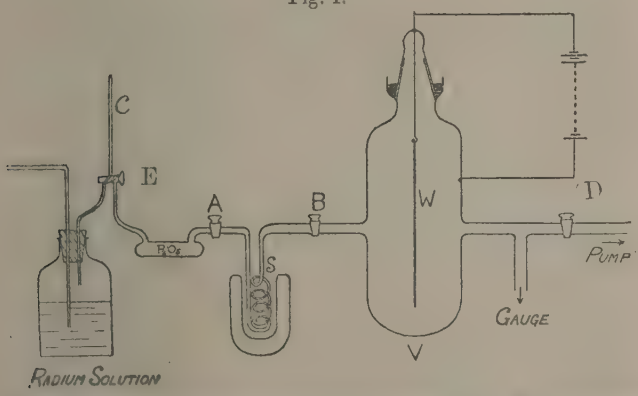
The results in the case of air show that the activity of the cathode is considerably greater than that of the anode, but that they approach equality as the lower pressure is reached.

This effect is more marked in sulphur dioxide, while for hydrogen no such difference in activity is observed, just as much active deposit being transmitted to the anode as to the cathode over this range of pressure.

Methods of Experiment.

A comparison was first made between the amounts of excited activity obtained on a wire maintained at 200 volts acting as cathode and then as anode over a range of pressure extending from ·01 mm. to 1·2 mm.

Fig. 1.



The apparatus used is represented in fig. 1. A brass wire W 10 cms. long, ·55 mm. diameter, on which the active

deposit was obtained, was suspended so as to hang symmetrically within the glass vessel V which was silvered on the inside, connexion to a battery of cells being made by means of a piece of platinum fused in the side of the vessel.

The usual method of experimenting was as follows:—

The whole system, with the exception of the vessel containing the radium emanation evolved from a solution of radium bromide, was exhausted firstly by means of a Fleuss pump and then by a charcoal tube immersed in liquid air (not shown in diagram). When the desired pressure had been obtained the tap D was closed, and by turning the tap E the small capillary tube C (·2 c.c. volume) was filled with the emanation at atmospheric pressure.

The tap B was then closed and the glass spiral S surrounded by liquid air, E was then turned and the emanation contained in the capillary C was allowed to pass over a tube containing P_2O_5 for drying purposes, after which it condensed in the spiral S.

A few trials showed that nearly all of the emanation had condensed in 15 minutes. The tap A was then closed, B opened, the liquid air removed from the spiral, and the emanation allowed to diffuse into the vessel V and a McLeod gauge which was in connexion with it. The resulting pressure was then read.

As the volume of the P_2O_5 tube was several times that of the spiral, quite low pressures were obtainable in the spiral although the capillary C had been filled at atmospheric pressures. The wire W was made either a cathode or anode as desired and exposed to the emanation for 1 hour. It was then removed from the vessel V, and its activity tested in the usual way by making it the central electrode of a cylinder connected with a Dolezalek electrometer and measuring the ionization produced by the α rays emitted from it. The electrometer leak obtained in a measured interval of time 14 minutes after the removal of the wire from the emanation was taken as a measure of the activity obtained on the wire.

The variation in activity with change of pressure is seen from Table I., also from fig. 2, where the abscissæ represent pressures and the ordinates the corresponding activities of the wire. It will be seen from the diagram that there is a

TABLE I.

Positive Electrode.		Negative Electrode.	
Pressure in mms.	Activity.	Pressure in mms.	Activity.
·011	69	·006	142
·013	79	·008	189
·137	84	·102	173
·202	81	·125	157
·250	62	·476	425
·608	63	·739	736
·792	67	1·165	1118
·865	56	**Neutral Electrode.**	
·922	56	Pressure in mms.	Activity.
1·102	57	·152	72
		·435	64
		·722	57
		1·140	62

very large decrease in the activity of the cathode as the pressure is diminished, while the anode shows if anything a small increase; the amount obtained by diffusion alone, *i. e.* to a neutral rod, being practically constant over this range of pressure.

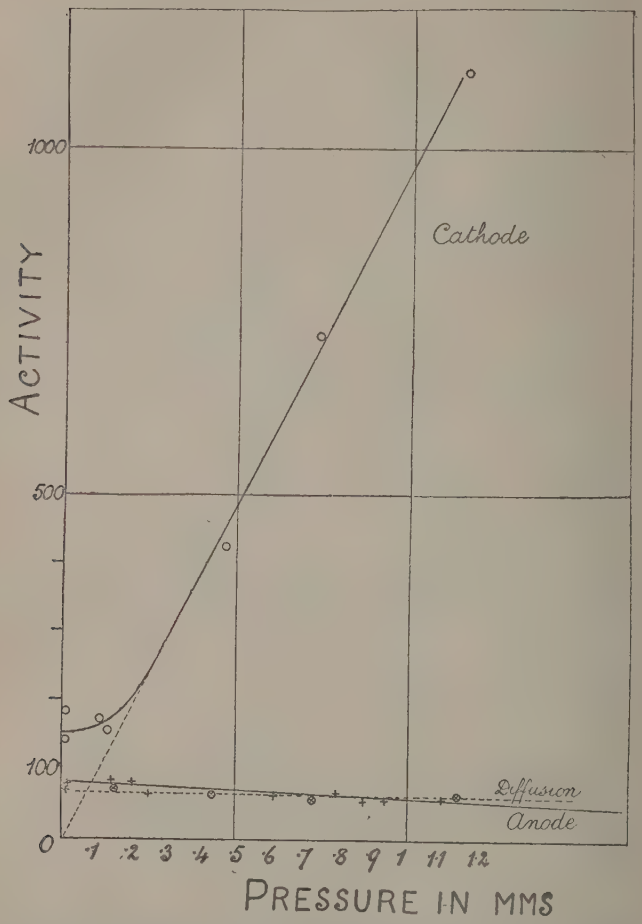
It will be observed that whereas at a pressure of about 1 mm. the activity of the cathode is about 20 times that of the anode, at ·01 mm. it is only about twice as much.

At this stage of the work it was decided to compare the activities of the cathode and anode at much higher pressures.

Several trials with the apparatus just described were made at pressures higher than 1 cm., but discordant results were obtained. This was probably due to the emanation being blown back into the spiral on allowing air to enter the vessel V, which was initially well exhausted as in the previous experiments.

For this reason observations were made with a modified system consisting simply of a brass cylinder down the centre of which passed a brass rod (provided with end-pieces to ensure uniformity of field) which was connected to cells giving

Fig. 2.



the same voltage as before. The brass cylinder was connected on one side with a small vessel which was filled with the emanation at atmospheric pressure, and on the other with a pump and pressure-gauge.

The small vessel containing the emanation was provided with metal electrodes, and the precaution was taken of applying a strong electric field to the emanation before letting

it into the brass vessel; this removed any active deposit or dust particles.

The system was initially exhausted to about 1 mm. pressure, the emanation then let in and the small vessel isolated from the cylinder, the pressure in which was then adjusted to whatever value was required. The activity obtained on the brass rod after one hour's exposure was measured in exactly the same way as before. Observations were made for a range of pressure extending from 2 mms. to 10 cms. The numerical data are contained in Table II., and the results shown graphically in fig. 3, where abscissæ denote pressures and ordinates the corresponding activities.

TABLE II.

Positive Electrode.		Negative Electrode.	
Pressure in cms.	Activity.	Pressure in cms.	Activity,
·13	152	·13	780
·27	140	2·04	1360
·55	163	2·70	1400
·63	148	7·22	1540
1·10	120	7·80	1470
3·78	94	Neutral Electrode.	
6·24	79	Pressure in cms.	Activity.
7·30	77	·36	219
8·94	77	·40	198
10·96	75	3·14	287
		3·74	300
		8·44	447
		8·82	437

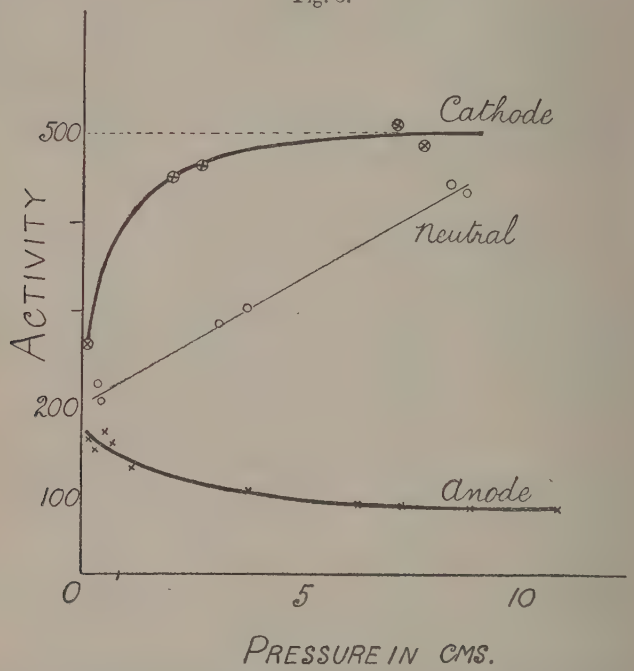
It will be seen that whereas the activity of the cathode *decreases* with diminishing pressure, there is a very marked *increase* in the activity of the anode, while the amount of active deposit that diffuses on to the neutral rod decreases very considerably as the pressure is reduced.

Diffusion experiments similar to those just cited are at

present being made, in which, however, other metals than brass are used as containing-cylinder and rod.

It will be seen from fig. 3 that at a pressure of about 2 mms. the quantity of active deposit transmitted to the anode is approximately equal to that diffusing on to a neutral pole.

Fig. 3.



The activity of the cathode being much larger than the anode, the scale in fig. 3 for the cathode is one third that for the anode and neutral pole.

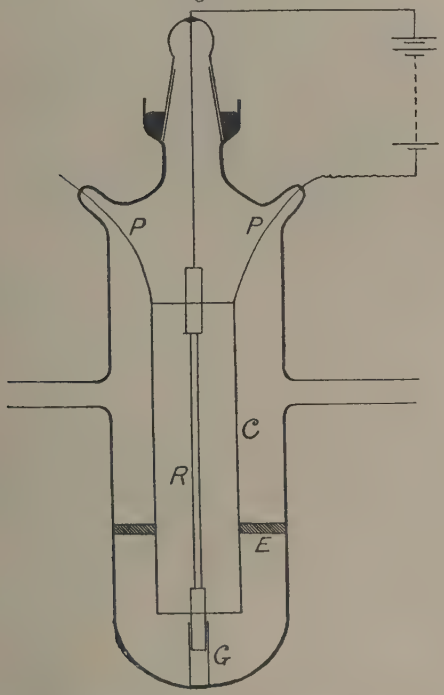
Now the active deposit that diffuses on to a neutral pole we have seen to be in the main positively charged (the bulk of it going to a cathode in an electric field). Very little of this positively charged matter can make its way to the anode. In order to account for the quantity obtained on the anode we are led to the conclusion that some at least of the active deposit particles that make their way to the anode are negatively charged.

The above results then go to confirm the view held by

Rutherford already referred to, that the active deposit particles which are directed to the anode have a negative charge.

It has been suggested by Rutherford*, in explanation of his results with thorium emanation, that the decrease in activity of the cathode as the pressure is reduced is due to a decreasing number of collisions between the active deposit

Fig. 4.



particles and the gaseous molecules with which they are mixed.

At the moment of expulsion of an α particle from the emanation atom, the residue, *i. e.* the active deposit particle, acquires a velocity in the opposite direction, which, though small compared with that of the α particle, is high compared with the velocity of an ordinary gaseous molecule.

* 'Radioactivity,' p. 319.

On the view above cited a certain number of collisions with the gas molecules is necessary to sufficiently reduce the velocity of the active deposit particles in order that moderate electric fields may direct them to cathode or anode.

Hence we might expect the effectiveness of a molecular encounter to depend on the nature of the gaseous molecules with which the active matter is associated. Experiments to test this point were therefore made with three gases differing considerably in molecular constitution, namely, air,

TABLE III.

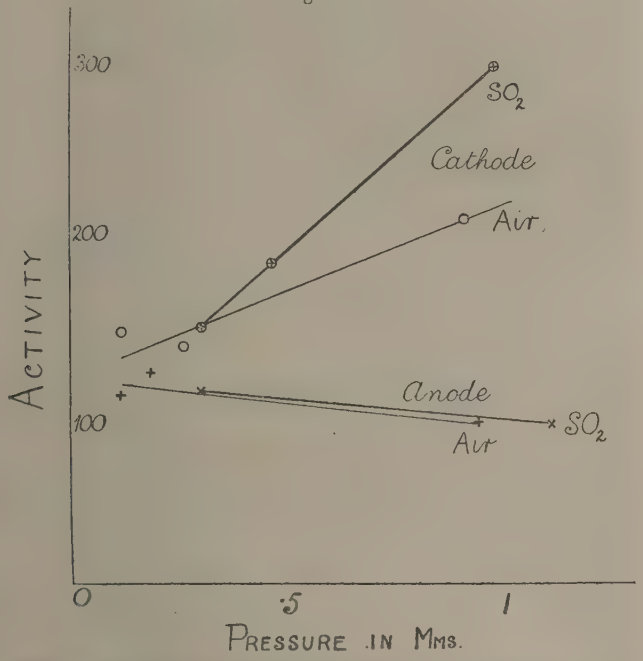
Air.			Sulphur Dioxide.		
Sign of Electrode.	Pressure in mms.	Activity.	Sign of Electrode.	Pressure in mms.	Activity.
Positive.	·115	108	Positive.	·302	111
,,	·185	122	,,	1·120	93
,,	·931	95	,,	...	...
Negative.	·115	146	Negative.	·297	148
,,	·260	137	,,	·462	184
,,	·902	211	,,	·970	298

Hydrogen.		
Sign of Electrode.	Pressure in mms.	Activity.
Positive.	·084	184
,,	·481	200
,,	·828	194
Negative.	·116	212
,,	·131	198
,,	·462	192
,,	·925	202
,,	·970	239
,,	1 080	188

hydrogen, and sulphur dioxide, and a comparison between the activities of cathode and anode over a range of pressure extending from ·1 mm. to 1 mm. was made with the low pressure system already described. The silvered vessel was, however, replaced by another glass vessel containing two concentric cylinders as seen in fig. 4 (p. 217).

The inner one R, 7 cms. long and ·36 cm. diameter, acted as the rod upon which the active deposit was obtained, C the outside cylinder, 8·95 cms. long and 2·7 cms. diameter, being suspended by two platinum wires PP which were sealed into the glass vessel and connected to either pole of the battery as required. The ebonite ring E kept the outer cylinder steady, and the rod R was supplied with a guard-ring at each end, one of which fitted into a glass tube G, thus serving to keep the rod central within the cylinder C.

Fig. 5.

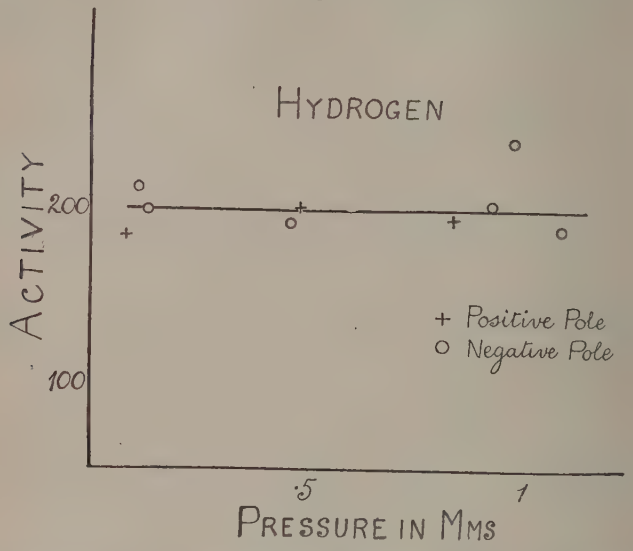


These modifications were adopted so as to ensure a uniform electric field between the rod and cylinder, and also to render the problem more accessible to mathematical treatment, the areas of the rod and cylinder being not very different. With this arrangement experiments with the gases already mentioned were made, and the results obtained are collected in Table III. and reproduced graphically in figs. 5 and 6.

It will be seen that for SO_2 there is a much greater difference in the activities of cathode and anode than is the case for air, while for hydrogen practically no difference in activity over the same range of pressure was obtained.

We should expect that the curves for cathode and anode in the case of hydrogen would show a divergence at higher

Fig. 6.



pressures, for if an encounter between the active deposit particle and a hydrogen molecule is not so effective in reducing the velocity of the former as a sulphur dioxide molecule, then we shall require a higher pressure with hydrogen to observe the same effects as with sulphur dioxide.

Thorium and Actinium.

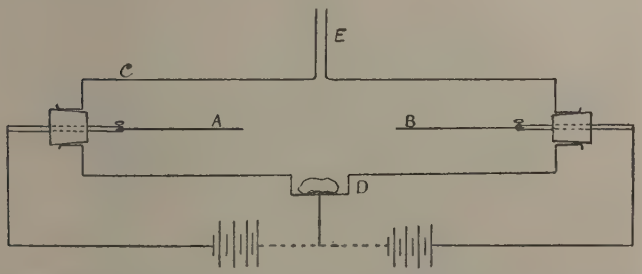
A few experiments made with the emanations from thorium and actinium show a rather striking difference in the distribution of their active deposits in an electric field.

The experimental arrangement seen in fig. 7 was used.

Two thin brass wires 7·5 cms. long and ·7 mm. diameter were made to lie along the axis of a brass tube C 30 cms.

long and 4·2 cms. diameter. This tube was fitted with a small capsule D, into which was placed a small quantity of thorium oxide, or of a preparation of actinium kindly lent me by Professor Rutherford.

Fig. 7.



The wire A was connected to the positive, B to the negative pole of a battery giving 320 volts, the brass tube being connected to the middle point.

The exit-tube E was connected to a Fleuss pump and a set of tubes containing calcium chloride and cotton-wool, thus ensuring a supply of dry and dust-free air.

When experimenting with thorium the wires were exposed to the emanation for 24 hours, after which they were removed and their activities tested with an electrometer in the manner already described.

The ratio of the activities of the cathode and anode at atmospheric pressure was found to be about 200 : 1; on reducing the pressure to 2 mms. the ratio was diminished to 25 : 1, this reduction being mainly due to the decrease in activity of the cathode already observed by Rutherford (*loc. cit.*). No certain increase in the very small activity of the anode was observed.

In the experiments with actinium the wires were exposed usually for about 2 hours.

At atmospheric pressures the ratio of the activities of the cathode and anode was about 2 to 1, while at 2 mm. pressure it was 22 to 1, the *increase* in the ratio being mostly due to an increase in the activity of the cathode. The active deposit on the two wires decayed at the same rate, namely, that of actinium A.

These results show that while the greater part of the active deposit from actinium emanation has a positive charge, yet at amospheric pressure a very considerable fraction has a negative charge, and is therefore directed to the anode.

For purposes of comparison the activities obtained on a wire when exposed to the emanations of Ra, Th, and Ac at atmospheric pressure are tabulated.

	Wire charged negatively.	Wire charged positively.
Thorium	200	1
Radium	200	10
Actinium	200	100

Conclusion.

In view of the different distributions in an electric field of the active deposits of thorium, radium, and actinium, it is difficult to think of the whole series of events between the formation of the active deposit and its transference to either electrode, as taking place in an exactly similar fashion.

It has been shown by Miss Slater* that slowly moving β particles accompany the α particles which are ejected from thorium and radium emanations. If there are two such β particles to every α particle, the remainder of the emanation atom, *i. e.* the active deposit, would be left with a positive charge.

This supposition would explain the almost complete transference of the active deposit of thorium to the cathode: but the small, though quite definite, quantity of the active deposit of radium that is directed to the anode still presents a difficulty. It may be that a few of the active deposit particles *gain* negative ions from the gas in which they are moving, which must be present in very large numbers.

In the case of actinium, although at a pressure of a few millims., far more activity is observed on the cathode than on the anode, as has already been found by Debierne†, yet we have seen that at higher pressures this inequality is very

* Phil. Mag. Oct. 1905.

† *Comptes Rendus*, vol. cxxxvi. p. 671.

much reduced, there being almost as many negative carriers as positive.

It is hoped that a more extended series of observations may throw some light on the apparently anomalous behaviour of actinium.

In conclusion, I desire to thank Professor Rutherford for several suggestions during the latter part of the work. The research was begun with Mr. Makower, who, however, could not continue the collaboration owing to pressure of other work. I wish to express my thanks for the very considerable help he has given me in these experiments.

Note added March 17th.

Some recent experiments made with actinium tend to explain the anomalous behaviour referred to above. A preparation of actinium was placed at the bottom of a cylinder, and two parallel plates were suspended so as to hang vertically above it. These plates were connected to the terminals of a battery of 300 volts, and after an exposure at atmospheric pressure usually lasting several hours the activities of the two plates were compared by means of an electroscope. The distance of the plates from the actinium preparation could be altered as required.

As already observed in the experiments described, the activity of the cathode was always greater than that of the anode.

It was found that when the plates were fixed at a distance of 4 cms. from the actinium, the ratio of the activity of the cathode to that of the anode was about 5 to 1; on bringing the plates nearer to the actinium this ratio rapidly increased, and when the distance was reduced to 2 mms. the activity of the cathode was more than a hundred times that of the anode.

These observations and others of a similar nature at different pressures (details of which it is hoped will appear in a future number), indicate that the sign of the electrical charge exhibited by the active deposit particles is some function of the distance which they have travelled through the containing gas, before reaching the electrodes.

Discussion.

Dr C. H. Lees expressed his interest in the paper, referring especially to the fact that the amount of active deposit which diffused onto a neutral rod varied with the pressure.

The Chairman referred to the radioactivity of the atmosphere, and remarked that the Author's experiments might be of use to meteorologists in enabling them to settle the question of the source of the radioactivity. He expressed his interest in the results obtained with actinium.

Mr Russ, in reply to Dr Lees, said that the fact that the quantity of active deposit on a neutral rod varied with the pressure was being investigated mathematically by Mr Bateman. With regard to the Chairman's remarks he observed that the source of the radioactivity of the atmosphere was an interesting question. The radioactivity due to thorium presented more difficulties than that due to radium because of the long life of the radium emanation. He suggested that the results might be due to the active deposits themselves which had longer lives than the emanations.

XII. *Note on certain Dynamical Analogues of Temperature Equilibrium.* *By* Prof. G. H. Bryan, *M.A.*, *F.R.S.* (*Bangor*) *.

In the *Archives Néerlandaises* for 1900 (Livre jubilaire dédié à M. H. A. Lorentz) I described under the title of "Energy Accelerations" a method of studying problems dealing with the partition of energy in systems of particles in which some kind of statistical equilibrium exists. This method consists essentially in writing down expressions for the second differential coefficients with respect to the time of the squares and products of velocities or momenta of the system considered.

The method in question appears to have been previously employed by Mr. Burbury, who, however, did not employ the term "energy-accelerations" in connexion with the second differential coefficients in question.

I was, and still am, of opinion that a further study of energy-accelerations must have an important bearing on all

* Read March 13, 1908.

problems in the Kinetic Theory dealing with questions of temperature-equilibrium, and the fact that no attempt seems to have been made to follow the problem up, may be taken as evidence of the large congestion of unsolved problems which presses heavily on the shoulders of the mathematician of to-day. The present note deals with two simple applications which happened to remain unnoticed when the paper was written.

Consider in the first place an ideal medium formed of material particles uniformly distributed in space, both as regards position and as regards direction, and attracting or repelling one another according to any law of force as a function of the distance between them.

If we confine our attention to one particular particle, the effect of the other particles will be to produce varying fields of force acting on the particle in question. Take now the equation of energy-accelerations which may be written in the more general form :—

$$\frac{d^2}{dt^2}\left(\tfrac{1}{2}mu^2\right) = \frac{1}{m}\left(\frac{d\mathrm{V}}{dx}\right)^2 - u\frac{d^2\mathrm{V}}{dt\,dx} - u^2\frac{d^2\mathrm{V}}{dx^2} - uv\frac{d^2\mathrm{V}}{dx\,dy} - uw\frac{d^2\mathrm{V}}{dx\,dz},$$

where u, v, w stand for velocity components, V the potential of the field due to the other particles.

The assumption that the field produced by the other particles is independent of the motion of the particle under consideration, and that this field has on an average no directional properties, shows that the mean values of the last two terms vanish, and the assumption that a stationary state exists requires that the mean value of the term $u d^2\mathrm{V}/dt\,dx$ should also vanish, reducing the energy-acceleration equation in this case to the ordinary standard form, brackets denoting mean values :—

$$\left[\frac{d^2}{dt^2}\left(\tfrac{1}{2}mu^2\right)\right] = \frac{1}{m}\left[\left(\frac{d\mathrm{V}}{dx}\right)^2\right] - \left[u^2\right]\left[\frac{d^2\mathrm{V}}{dx^2}\right].$$

For energy equilibrium the left-hand side must vanish. This is only possible when the mean value of $d^2\mathrm{V}/dx^2$ is positive. Now the assumed absence of directional properties,

or in other words the assumed isotropic character of the medium, requires that the average values of d^2V/dx^2, d^2V/dy^2, and d^2V/dz^2 shall be equal ; therefore each is equal to one-third the average value of ΔV. We conclude that statistical energy equilibrium cannot exist in a system of particles possessing the assumed properties unless ΔV is positive.

For the Newtonian law of force $\Delta V=0$. In this case the mean value $[d^2V/dx^2]$ therefore also vanishes, and the energy-acceleration equation takes the form :—

$$\left[\frac{d^2}{dt^2}(\tfrac{1}{2}mu^2)\right]=\frac{1}{m}\left[\left(\frac{dV}{dx}\right)^2\right].$$

This shows that the only kind of statistical equilibrium is the statical state of unstable equilibrium defined by $dV/dx=0$, $dV/dy=0$, and $dV/dz=0$ on each particle, and in the absence of this state an acceleration of kinetic energy will take place.

It is thus impossible with the Newtonian law to build up a medium of material particles, either attracting or repelling one another, and possessing properties of energy equilibrium analogous to those of a system of gas molecules.

It need not be pointed out that this investigation does not preclude the possibility under the Newtonian Law, of stationary motions such as those occurring in the solar system.

Exactly the same conclusions hold good if the law of force is such as to make ΔV negative. The equations of energy equilibrium here require the further condition that $[u^2]$ $[r^2]$ $[w^2]$ should be zero, which can only happen if the system always remains at rest.

The necessary condition $\Delta V>0$ becomes, for the particular case in which the field is due to an attracting particle placed at the origin,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dV}{dr}\right)>0,$$

showing that r^2dV/dr must increase with r. In other words, the force if repulsive must vary according to a higher power

of the inverse distance than the square (the inverse fifth power would represent a possible law of force if repulsive). If the force is attractive it must vary according to a lower power of the inverse distance than the square.

The second point to be noticed is that unless the expression for the kinetic energy of a dynamical system is a quadratic function of the velocities with *constant* coefficients, the equations of energy equilibrium no longer assume the form of linear relations connecting the mean squares and products of velocities, but they also involve terms of the fourth degree in these velocities. An illustration of this fact is afforded by the motion of a particle in a plane when referred to polar coordinates. If we write down the expressions for the energy-accelerations

$$\frac{d^2}{dt^2}(\tfrac{1}{2}\dot{r}^2) \quad \text{and} \quad \frac{d^2}{dt^2}(\tfrac{1}{2}r^2\dot{\theta}^2)$$

in terms of the velocities and coordinates, using the equations of motion

$$\ddot{r} - r\dot{\theta}^2 = -\frac{dV}{dr} \quad \text{and} \quad \frac{1}{r}\frac{d}{dt}(r^2\dot{\theta}) = -\frac{dV}{rd\theta}$$

we shall obtain expressions involving the velocity components up to the fourth degree, and the energy components therefore up to the second degree. The conditions of energy equilibrium between the transversal and radial components will therefore no longer take the form of linear relations connecting the mean values of the energy components in question.

On the other hand, when we refer the motion to x and y coordinates, the equations of energy equilibrium are linear in the energy components.

It appears, therefore, that if dynamical systems are to represent the phenomena of temperature-equilibrium consistently with the commonly accepted hypothesis that temperature is a quantity of the nature and dimensions of molecular kinetic energy, the expression for the kinetic energy must in general have constant coefficients or must at least satisfy certain conditions which are fulfilled in the case of constant

coefficients. While the analogy of kinetic energy with temperature may hold good in the case of a system of particles, there must exist dynamical systems for which this analogy does not hold good. As a purely negative conclusion this result is not inconsistent with Stefan's law in which we have the energy of radiation proportional to the fourth power of the energy of molecular motion. But whether it is possible to construct a dynamical model whose energy-partition is analogous to Stefan's Law, must be a question for future investigation.

Discussion.

Prof. Cassie discussed the method and results of the paper, and remarked that the results of experiments appeared to indicate that the forces between particles varied with the distance according to some law more rapid than the inverse fifth power.

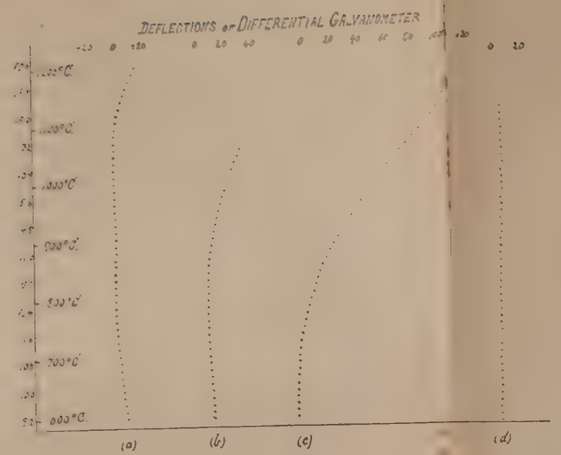
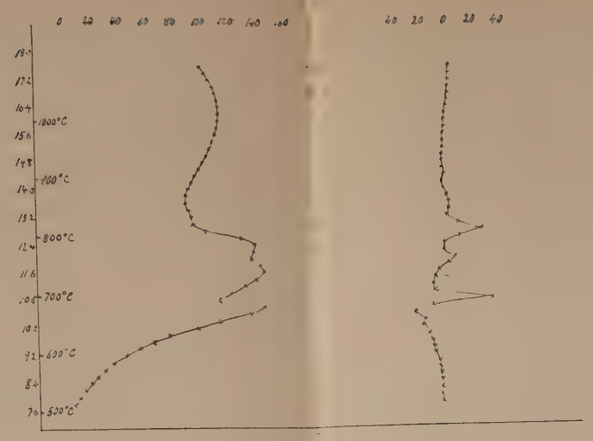
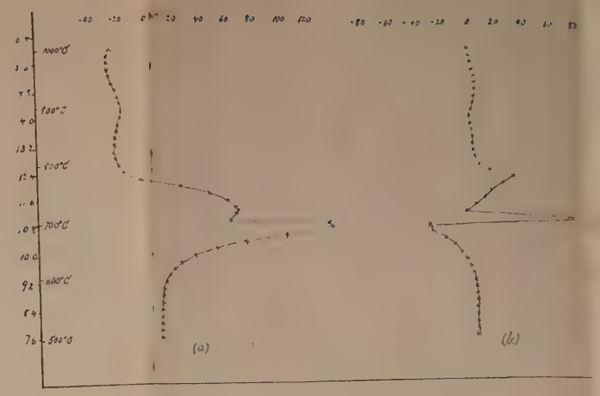


FIG 7.



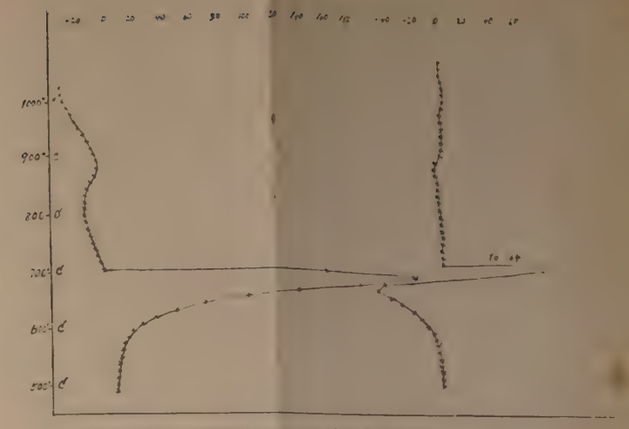
DIFFERENTIAL AND DERIVED DIFFERENTIAL COOLING CURVES OF STEEL
(0·20% CARBON.)
SLOW COOLING (1 HOUR 45 MINUTES).

FIG 8.



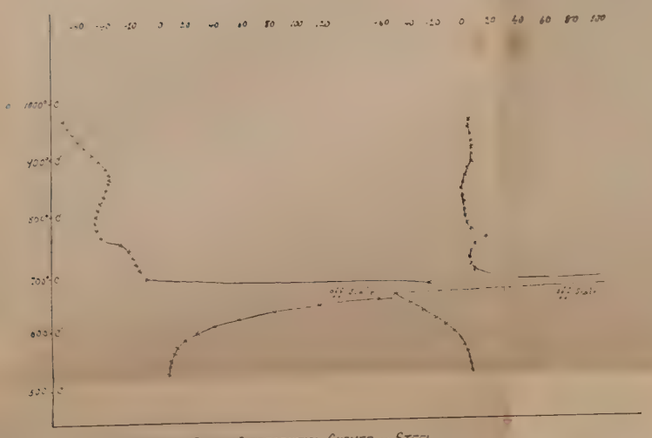
DIFFERENTIAL AND DERIVED DIFFERENTIAL CURVES OF STEEL
(0·32% CARBON)

FIG. 9.



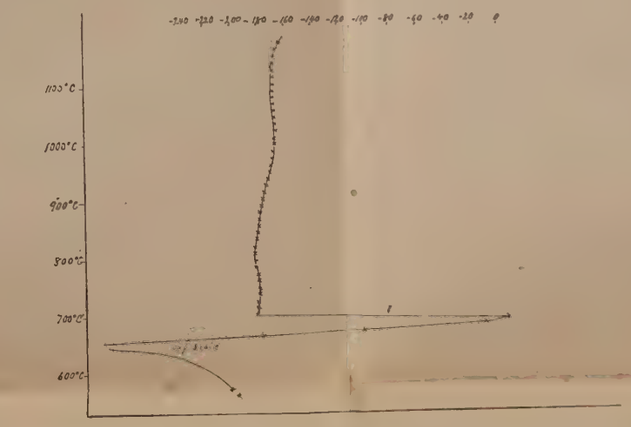
DIFFERENTIAL AND DERIVED DIFFERENTIAL CURVES OF STEEL
(0·94% CARBON)

FIG 10.



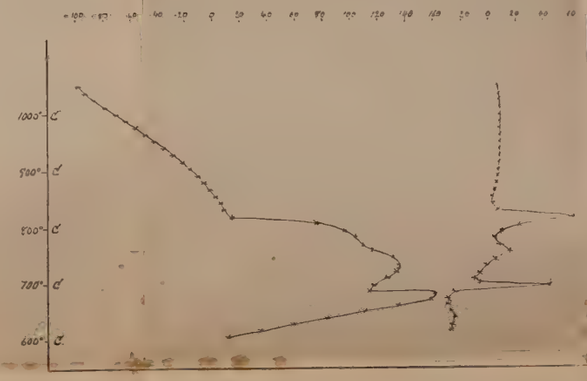
DIFFERENTIAL AND DERIVED DIFFERENTIAL CURVES OF STEEL
(1·26% CARBON)

FIG. 11



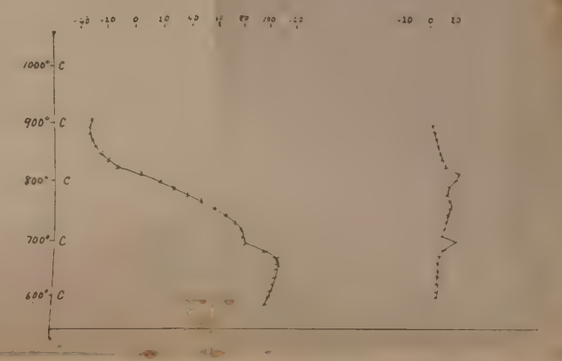
DIFFERENTIAL CURVE OF TWO PIECES OF STEEL
(CARBON 0·99%)

FIG. 12.



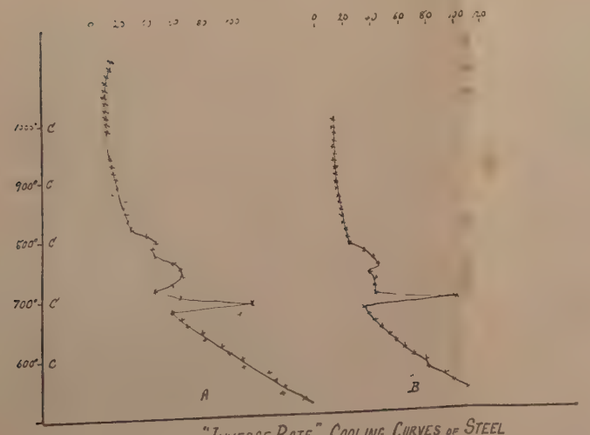
DIFFERENTIAL AND DERIVED DIFFERENTIAL CURVES OF STEEL
RAPID COOLING - 25 MINUTES (CARBON 0·20%)

FIG. 13.



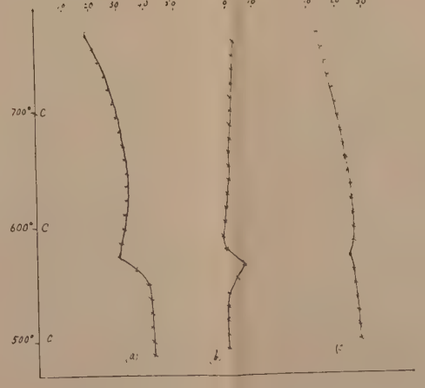
DIFFERENTIAL AND DERIVED DIFFERENTIAL CURVES OF STEEL
VERY RAPID COOLING - 12 MINUTES (0·20% CARBON)

FIG. 14.



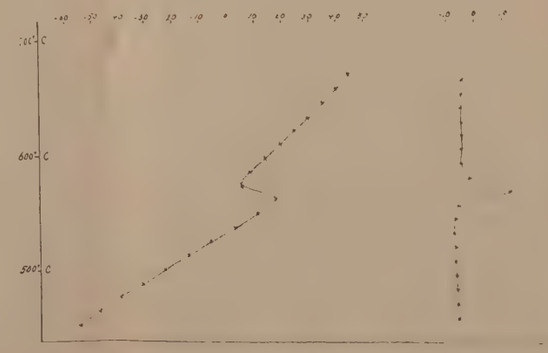
"INVERSE RATE" COOLING CURVES OF STEEL
(CARBON:- A - 0·90% B - 0·32·6%)

FIG. 15.



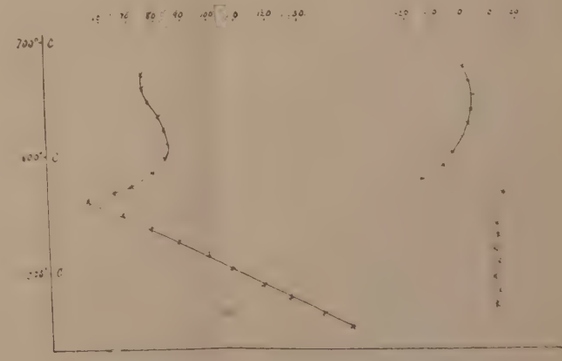
DIFFERENTIAL HEATING (a) AND COOLING (b) CURVES OF N.P.L. ELECTRIC FURNACE
(c) DIFFERENTIAL COOLING CURVE OF MACINTYRE PORCELAIN

FIG 16



DIFFERENTIAL AND DERIVED DIFFERENTIAL HEATING CURVE OF "SILVER SAND"

FIG 17



DIFFERENTIAL AND DERIVED DIFFERENTIAL COOLING CURVE OF "SILVER SAND"

FIG. 18.

THE

PHYSICAL SOCIETY OF LONDON.

MEMORANDUM OF ASSOCIATION.

1. The name of the Society is "The Physical Society of London."

2. The registered Office of the Society will be situated in England.

3. The objects for which the Society is established are to promote the advancement and diffusion of a knowledge of Physics and for this purpose especially :—

(1) To invite from the Members and others, communications, written or oral, relating to Physics, and to receive, hear and discuss such communications at Meetings of the Society.

(2) To invite the exhibition of and to exhibit, at Meetings of the Society, any new, improved or other apparatus for Physical research, and any new or other experiments illustrative of Physical laws or phenomena.

(3) To print and publish, and to sell, lend and distribute any communications made to the Society, or any other papers, treatises, or communications relating to Physics, and any

reports of the proceedings and accounts of the Society, and for this purpose to cause translations to be made of any such papers, treatises, or communications as shall be in a foreign language, and to illustrate any of the publications.

(4) To purchase, take on lease or otherwise acquire, and also to dispose of, any premises and other property for the purposes of the Society, subject to the provisions of Sect. 21 of the Companies Act 1862.

(5) To do all such other lawful things as are incidental or conducive to the attainment of the above objects.

4. The income and property of the Society whencesoever derived shall be applied solely towards the promotion of the objects of the Society as set forth in this Memorandum of Association; and no portion thereof shall be paid or transferred directly or indirectly by way of dividend or bonus or otherwise howsoever by way of profit to any person who is or has been a Member of the Society, or to any person claiming through him, provided that nothing herein contained shall prevent the payment of just remuneration to any officers or servants of the Society or to any one although a Member of the Society for services rendered to the Society.

5. The fourth paragraph of this Memorandum is a condition on which a license is granted by the Board of Trade to the Society in pursuance of Sect. 23 of the Companies Act 1867. For the purpose of preventing any evasion of the terms of the said fourth paragraph, the Board of Trade may from time to time, on the application of any Member of the Society, impose further conditions which shall be duly observed by the Society.

6. If the Society act in contravention of the fourth paragraph of this Memorandum or of any such further conditions, the liability of every Member of the Council of the Society shall be unlimited, and the liability of every Member of the Society who has received any such dividend, bonus, or other profit as aforesaid shall likewise be unlimited.

7. Every Member of the Society undertakes to contribute to the assets of the Society in the event of the same being wound up during the time that he is a Member, or within one year afterwards, for payment of the debts and liabilities of the Society contracted before the time at which he ceases to be a Member, and of the costs, charges, and expenses of winding up of the same, and for the adjustment of the rights of the contributories amongst themselves, such amount as may be required not exceeding one pound, or, in case of his liability becoming unlimited, in pursuance of the last preceding paragraph of this Memorandum, such amount as may be required, provided always that every Member of the Society whose liability remains limited, shall be called on to contribute to the full extent of his liability before any greater contribution is made by any Member of the Society whose liability has become unlimited.

8. If upon the winding-up or dissolution of the Society there remains after the satisfaction of all its debts and liabilities any property whatsoever, the same shall be applied in the first place to the reimbursement of Members who may have made payments under the provisions of the last preceding paragraph, and the surplus shall not be paid to or distributed among the Members of the Society, but shall be given or transferred to some other institutions or institution having objects similar to the objects of the Society, to be determined by the Members of the Society at or before the time of dissolution, or in default thereof by such Judge of the High Court of Justice as may have or acquire jurisdiction in the matter.

We, the several persons whose names and addresses are subscribed, are desirous of being formed into a Society in pursuance of this Memorandum of Association.

Names, Addresses, and Descriptions of Subscribers.

1.

2.

3

4.

5

6.

7

*Dated*_____ _____ 1877.

Witness to the above signatures:

ARTICLES OF ASSOCIATION

OF

The Physical Society of London.

[*As altered by Special Resolution on May* 22, 1908, *and confirmed on June* 12, 1908.]

WHEREAS, in the year 1874, certain persons desirous of promoting the objects described in the Memorandum of Association formed themselves into a Society called "THE PHYSICAL SOCIETY OF LONDON," and adopted certain Bye-laws for the Government of the said Society, wherein (as subsequently altered and modified) are contained (*inter alia*) provisions for the appointment of certain officers and members of a Council, and provisions that Members of the said Society should pay an annual subscription of £1, and that any Member might compound for his annual subscription by the payment of £10 in one sum:

AND WHEREAS the said Society (hereinafter called the original Society) has continued its operations until the present time, and the persons whose names and addresses are set forth in the first schedule hereto are now the Members of the Council, and hold the respective offices in the said Schedule mentioned, and the persons whose names and addresses are set forth in the second Schedule hereto are the present Members of the original Society, and such of them as have this mark || set against their names in the said second Schedule have compounded for their annual subscriptions:

AND WHEREAS it is intended that the original Society shall be registered and incorporated under the Companies Acts 1862 and 1867 as an association falling within the 23rd Section of the Companies Act 1867, and that the Members thereof shall accordingly become Members of this Society:

AND WHEREAS the license of the Board of Trade required by the said 23rd Section of the Companies Act 1867 has been duly granted:

NOW IT IS AGREED AS FOLLOWS :—

1. The Society is established for the purposes expressed in the Memorandum of Association.

2. The Regulations contained in these Articles and in the Memorandum of Association are substituted for the Bye-Laws of the original Society.

3. These Articles shall be construed with reference to the provisions of the Companies Acts 1862 and 1867, and terms used in these Articles shall be taken as having the same respective meanings as they have when used in those Acts. In these Articles words importing the masculine gender only, shall be taken to include the feminine gender.

4. For the purposes of registration the number of the Members of the Society is declared not to exceed 1000.

Fellows.

5. The Society shall consist of Fellows, *ex officio* Fellows, Honorary Fellows, and Students.

6. No *ex officio* Fellow, Honorary Fellow, or Student shall, by reason of his being legally a member of the Physical Society within the meaning of the Companies Acts, be entitled to any privileges other than those which by these Articles attach to the specific class of members to which he belongs.

7. The persons whose names are set forth in the second Schedule hereto as Fellows, and any other persons who shall be elected Fellows, as hereinafter provided, shall be Fellows of the Society.

8. The Presidents for the time being of such Societies as the Council may from time to time recommend, may, with the approval of a General Meeting of the Society, be elected as *ex officio* Fellows. They shall receive all the publications issued by the Society during their term of Fellowship, and enjoy all other privileges of Fellows, but shall not be liable to pay any subscription.

9. Honorary Fellows shall be such persons distinguished for having advanced the Science of Physics, and not being British subjects, as shall be elected Honorary Fellows in the manner hereinafter provided.

10. The number of Honorary Fellows shall not exceed twelve at any one time, except with the sanction of a resolution of a General Meeting of the Society.

11. Fellows shall be entitled to a copy of all publications issued by the Society upon such terms as the Council or a General Meeting of the Society may from time to time fix, and to attend all its meetings. The rights and privileges of every Fellow, *ex officio* and Honorary Fellow shall be personal to himself; they shall not be transferable by his own act or by operation of law, and shall cease upon his death.

Election, Admission, Retirement, and Expulsion of Fellows.

12. No person shall be qualified for Election as a Fellow, except as hereinafter appointed, unless he be recommended as a Candidate by not less than three Fellows, to two of whom he must be personally known. Such recommendation shall be made by the signature of such Fellows to the following form :—

Name _____

Occupation or Qualification } _____

Residence _____

being desirous of becoming a Fellow of the PHYSICAL SOCIETY OF LONDON, We, the undersigned being Fellows, recommend him as a proper person to be elected into the Society.

Dated _____ *day of* _____ 19__ .

From personal knowledge. *From general knowledge.*

13. The names of Candidates so recommended shall be submitted to the Council hereinafter mentioned. The Council shall, at a subsequent Meeting, either approve or reject the same. The Council may in their discretion reject the name of any Candidate.

14. The Council may at their discretion recommend to the

Society for election as a Fellow any person not qualified according to Article 12, when, in the opinion of at least three-fourths of those present at the Council Meeting, circumstances render it desirable to do so.

15. The names of such Candidates as shall be approved by the Council shall be submitted to the Society at a Science Meeting held after such approval shall have been given; and for this purpose the names of the Candidates and of the Fellows who recommend them shall be read at such Meeting by one of the Secretaries. The names shall then be submitted for ballot at a later Science Meeting of the Society.

16. Honorary Fellows and *ex officio* Fellows shall be nominated by the Council. An Honorary Fellow or *ex officio* Fellow shall be deemed to be nominated by the Council when his name has been submitted to one Meeting of the Council and accepted upon ballot at a second Meeting thereof.

17. A list of the names of persons nominated by the Council as Honorary Fellows or *ex officio* Fellows shall be sent to every Fellow, by being posted to his registered address, at least fourteen days before the Annual General Meeting. The names shall then be submitted for ballot at the Annual General Meeting.

18. At every ballot, whether at a Meeting of the Council or at a General Meeting, one black ball in four shall exclude.

19. Every Fellow who is elected shall be informed of his election by one of the Secretaries, who shall also send him a copy of the Memorandum and Articles of Association of the Society, together with an obligation in the following form :—

"I, the undersigned, having been elected a Fellow (or *ex officio* or Honorary Fellow, as the case may be) of the Physical Society of London, do hereby engage that I will endeavour to promote the interests and welfare of the Society, and will observe its laws as long as I shall continue a Fellow thereof.

Signed

*Dated*_____*day of*_____ 19___.

20. Every person elected, whether as a Fellow, an *ex officio* or an Honorary Fellow, shall within one calendar month, or such extended or other time as the Council shall in any case direct, sign and return the said form to one of the Secretaries; and every person elected as a Fellow shall, within three calendar months from the date of his election, pay the entrance fee and the first annual subscription, of the amount hereinafter respectively mentioned.

21. If any Fellow shall fail to comply with so much of the last preceding Article as applies to his case, the Council may at any time after three calendar months from the date of his election, declare his election void.

22. At the first Science Meeting at which a Fellow is present after he has complied with the provisions of Article 20, he shall be admitted according to the following form:—He shall first sign his name in a book to be kept for that purpose, and shall then be presented to the President or other Fellow in the Chair by one of the Secretaries; and the President (or Chairman), addressing him by name, shall say, "In the name of the Physical Society of London, I admit you a Fellow thereof."

23. If any Fellow, after returning to the registered office all books or other property of the Society in his hands, shall leave at or send by post to the registered office a notice in writing signed by himself, stating that he resigns his membership in the Society, he shall thereupon cease to be a Fellow.

24. Upon the recommendation of the Council the Society may, by a resolution passed at a Special General Meeting, expel any Fellow from the Society, provided that at this Meeting not less than 20 Fellows shall be present and that of those who vote at least three-fourths shall be in favour of the resolution.

25. In any case in which the Council may think proper to recommend the expulsion of a Fellow, the President shall call a Special General Meeting to consider the matter. At such Meeting the voting upon the question shall be by ballot.

26. If any Fellow fails to pay his subscription within three calendar months of the same becoming due from him, the Treasurer shall serve him with notice that he is in arrear, and in

the event of non-payment within six calendar months from the date at which the subscription became due, he will be liable to be removed from the Society.

27. In the event of non-payment within such six calendar months, the Fellow so in arrear may be removed from the Society by a resolution of the Council to that effect.

28. The last two preceding Articles shall be additional to, and not in substitution for, the power given by Article 21.

29. No Fellow shall be entitled to any publications of the Society if his subscription be three calendar months or more in arrear.

30. Any Fellow, who shall retire, be expelled or removed from the Society, shall remain liable for the payment of all monies due from him at the date of his retirement, expulsion or removal.

Payments by Fellows.

31. The persons whose names are set forth in the second Schedule hereto, other than those whose names are marked thus ||, shall pay an annual subscription of £2 2*s.* each.

32. The persons whose names are marked thus || in the said second Schedule are Fellows who have compounded for their annual subscriptions. They shall not be liable to pay any further annual subscriptions.

33. Unless he be transferred from the class of Student, in which case no entrance fee or transfer fee shall be paid, every Fellow hereafter to be elected shall pay an entrance fee of £1 1*s.*, and an annual subscription of £2 2*s.*

34. Subscriptions shall be payable in advance, and shall become due on the 1st day of January in each year.

35. The entrance fee and subscription shall become due from every Fellow immediately upon his election; but any Fellow elected on or after the 1st of November in any year shall not be liable to pay his subscription for that year. For the purpose of subscriptions a year shall be the period between the 1st day of January and the 31st day of December.

36. Any Fellow may, at any time, compound for all annual subscriptions thereafter to become due from him. The composition fee shall be, for any Fellow who shall not

have already paid ten annual subscriptions, fifteen times the amount of the annual subscription payable by such Fellow, and for any Fellow who shall have already paid ten or more annual subscriptions, ten times the amount of the annual subscription payable by such Fellow.

37. The Council may, with the sanction of a Special Resolution, as defined in the Companies Act 1862, from time to time increase or reduce the annual subscription and the amount to be paid for compounding.

38. Neither *ex officio* nor Honorary Fellows shall be liable to pay any entrance fee, or annual or other subscription.

Students.

39. Students shall be persons not under eighteen years of age nor over twenty-two years of age. No person shall remain a Student for a longer period than three years.

40. No person shall be qualified for election as a Student unless he be recommended by a Fellow to whom he is personally known. Such recommendation shall be made by the signature of such Fellow to the following form:—

Name _____

Residence _____

being a Student at _____ in the subject

of _____ under _____

and being desirous of becoming a Student of the PHYSICAL SOCIETY OF LONDON, I, the undersigned, recommend him as a proper person to be elected into the Society.

Signature of Fellow _____

Dated _____ *day of* _____, 19 ___

The names of Candidates so recommended shall be submitted to the Council, who shall have power to elect such Candidates as seem to them desirable without reference to a Meeting of the Society.

41. The payment of fees and the resignation of membership in the case of Students shall be regulated by the Articles applying to Fellows, viz., Nos. 20, 21, 23, 26, 27, 28, 29, 30, and 34, so far as these are applicable without prejudice to the Articles here following.

42. Every Student shall pay an annual subscription of 10*s*. 6*d*.

43. The Council may, if they think proper, expel any Student from the Society, provided that at the meeting of Council not less than eight Members shall be present and that of those who vote not less than three-fourths shall be in favour of such a course.

44. Students shall receive a copy of the Proceedings and Bulletin when issued, and, on payment of a further annual sum of five shillings, shall be entitled to a copy of the Physics or Electrical Engineering section of 'Science Abstracts,' or on a payment of an annual sum of seven shillings and sixpence to a copy of both parts.

45. A Student desiring to be transferred from the class of Student to that of Fellow shall apply in the manner set forth in Article 12, stating on the form that the recommendation is for transfer.

Council.

46. The affairs of the Society shall be managed by a Council consisting of a President, not more than four nor less than two Vice-Presidents (exclusive of the *ex officio* Vice-Presidents presently mentioned), two Secretaries, a Foreign Secretary, a Treasurer, a Librarian, and not more than ten other persons all of whom must be Fellows of the Society.

47. The first Council shall be composed of the persons whose names and addresses are set forth in the first Schedule hereto, and they shall hold the several offices set opposite to their respective names therein.

48. Subsequent Councils shall be elected by the Society annually by ballot at the Annual General Meeting.

49. At each Annual General Meeting all the Members of the Council shall retire from office, and the Society shall elect a new Council in manner herein provided.

50. It shall be the duty of the Council before each Annual General Meeting to prepare a list containing the names of the Fellows whom they recommend for election to the respective offices of President, Vice-Presidents, Secretaries, Foreign Secretary, Treasurer, and Librarian, and the names of ten other Fellows whom they recommend for election as Ordinary Members of the Council.

51. Names recommended by the Council shall be names proposed at one Meeting of the Council and agreed to at a subsequent Meeting.

52. A copy of the list so prepared shall be sent to every Fellow by being posted to his registered address at least fourteen days before the Annual General Meeting.

53. Every Fellow shall have power to alter the list so sent by the removal or addition of the name of any Fellow, or as regards the name of any Fellow already included in the list by removing the same from the office for which the Fellow has been recommended by the Council, or inserting such name under a different office, and he shall use the list with such alterations (if any) as a balloting-list at the Annual General Meeting.

54. Any balloting-list, which (as altered) shall contain the names of more than one President, four Vice-Presidents, two Secretaries, one Foreign Secretary, one Treasurer, one Librarian, and ten Ordinary Members of Council, shall be null and void.

55. On the day of election the Chairman shall nominate two Scrutators, to be approved by the Meeting, to assist the Secretaries in examining the balloting-lists. Each Fellow present and voting shall deliver his list to one of the Scrutators. Fellows who are not able to be present may vote by sending their balloting-lists in a sealed envelope addressed to the Scrutators, enclosed in a letter addressed to the Secretaries at the registered Office of the Society, so as to be delivered before the time of meeting. The Fellows whose names shall be reported to the President by the Scrutators as having received the majority of votes for filling the offices of President, Vice-Presidents, Secretaries, Foreign Secretary, Treasurer, Librarian, and Ordinary Members of Council respectively,

shall be deemed to be elected to those several offices, and their names shall be announced from the Chair as those of the persons elected to serve for the ensuing year.

56. A retiring Member of the Council shall be eligible for re-election provided that—

(*a*) The same person shall not be eligible as President for more than two years in succession.

(*b*) At least three persons shall be elected to the new Council who were not Members of the retiring Council.

(*c*) No Ordinary Member of Council shall be eligible to serve in the same capacity for more than five consecutive years.

(*d*) In each year the Vice-President who has been longest in office shall retire and not be immediately eligible for re-election in the same capacity.

57. Any casual vacancy occurring in the Council may be filled up by the Council.

58. Every Fellow of the Society who has been President shall be an *ex officio* Vice-President and Member of the Council, in addition to the Members elected in manner aforesaid.

Meetings of the Society.

59. The Meetings of the Society shall be of two kinds—

(A) General Meetings, including Annual and Special General Meetings.

(B) Science Meetings.

60. The word "Meeting," when standing alone in these Articles, and referring to a Meeting of the Society, shall include as well a Science Meeting as a General Meeting, unless repugnant to the subject or context.

A. *General Meetings.*

61. General Meetings shall be held once in every calendar year and not more than 15 months after the holding of the last preceding general meeting at such time and place as may be prescribed by the Society in General Meeting; and, if no time and place is so prescribed, as may be determined upon by the Council.

62. The above-mentioned General Meetings shall be called Annual General Meetings; all other General Meetings shall be called Special General Meetings.

63. The President or the Council may whenever he or they think fit, and the President shall, upon receiving a written requisition made by not less than ten Fellows of the Society, convene a Special General Meeting.

64. Any such requisition shall state the object for which the Meeting is required, and shall be addressed to the President, and left at or sent by post to the registered office.

65. Upon receiving the requisition, the President shall forthwith convene a Special General Meeting, to be held within 14 days from the receipt of the requisition. If he do not so convene the same, the requisitionists or any other Fellows of the Society, not less than ten in number, may themselves convene a Special General Meeting.

66. Seven days' notice at the least, exclusive of the day of giving the notice, but inclusive of the day for which the notice is given, specifying the place, the day, and the hour of meeting, and in case of special business the general nature of such business, shall be given to each Fellow by circular posted to him at his registered address. Honorary and *ex officio* Fellows shall not be entitled to any notice.

67. All business shall be deemed special that is transacted at a Special General Meeting, and all that is transacted at an Annual General Meeting, with the exception of the consideration of the accounts, balance-sheets, and ordinary reports of the Council, Treasurer, and Auditors respectively, and business relating thereto.

68. No business, of which notice has not been given in manner aforesaid, shall be considered, discussed, or voted upon at a General Meeting.

69. At every General Meeting (except where by these Articles a larger quorum is expressly required) ten Fellows shall form a quorum. If at any General Meeting a quorum is not present within half an hour of the time appointed for holding the Meeting, the Meeting, if convened upon the requisition of Fellows, shall be dissolved. In any other

case it shall stand adjourned to the same day in the next week, at the same time and place; and if at such adjourned Meeting a quorum is not present, it shall be adjourned *sine die*.

70. The Chairman of any General Meeting may, with the consent of the Meeting, adjourn the Meeting from time to time, and from place to place.

71. Every Fellow shall have one vote. Neither *ex officio* nor Honorary Fellows nor Students shall have any vote.

72. Votes may be given either personally or by proxy, in such a form as may be from time to time prescribed by the Council.

73. At any General Meeting, unless a poll is demanded by at least five Fellows, a declaration by the Chairman that a resolution has been carried and an entry to that effect in the book of proceedings of the Society, shall be sufficient evidence of the fact, without proof of the number or proportion of the votes recorded in favour of or against such resolution.

74. If a poll is duly demanded, it shall take place at such time and place, and either by open voting or by ballot, as the Chairman directs, and the result of the poll shall be deemed the resolution of the Meeting at which the poll is demanded. The Chairman of a General Meeting shall, in case of an equality of votes at the Meeting, or at the poll if a poll is demanded, be entitled to a casting vote in addition to the vote or votes to which he is entitled as a Fellow.

B. *Science Meetings.*

75. The Council shall from time to time appoint the times and places for holding Meetings of the Society, to hear and discuss communications relating to Physics, and generally to proceed with the scientific business of the Society. The Meetings so appointed shall be called Science Meetings.

76. Science Meetings shall, unless the Council shall otherwise appoint, be held at least once in every calendar month during the months from November to June inclusive; and that period, or such other period as the Council shall from time to time appoint for holding such Meetings, is in these Articles referred to as a Session.

77. At any Science Meeting the names of Candidates for Fellowship may be read, new Fellows may be elected, and new Fellows admitted.

78. No notice shall be required of the business to be transacted at a Science Meeting.

79. Persons not Fellows of the Society may attend these Meetings as visitors upon the introduction of Fellows, Honorary Fellows, and *ex officio* Fellows. Each Fellow shall be at liberty to introduce not more than two visitors at any Science Meeting. The names of visitors, together with those of the Fellows introducing them shall be entered in a book kept for the purpose.

80. The Council may in their discretion grant to persons not Fellows of the Society admission to all or any of the Science Meetings of a Session.

81. At a Science Meeting the ordinary course of business shall, subject to the control of the Chairman, be as follows :—

(1) The Minutes of the previous Meeting shall be read and submitted for confirmation.

(2) New Fellows shall be admitted.

(3) Presents made to the Society since its last Meeting shall be announced from the Chair and exhibited when desirable.

(4) The names of candidates for election as Fellows shall be read.

(5) The ballot for new Fellows shall take place.

(6) The scientific business of the Meeting shall be proceeded with.

(7) The matter to be brought before the next Meeting shall be announced from the Chair.

82. Every person who shall desire to bring a communication before the Society shall give notice thereof in writing to one of the Secretaries, stating the nature of the communication. The Council shall decide whether such communication shall be accepted (*a*) for presentation at a Meeting and (*b*) for publication in full or in abstract.

83. Written or oral communications shall be accompanied

wherever it is practicable by experimental illustration, and the exhibition and use of the apparatus referred to in them.

84. All communications, except those merely published in title or abstract, which have been accepted by the Council, together with all necessary explanatory drawings, shall become the property of the Society. The Council shall have power to publish in the Proceedings of the Society and to communicate to any other journal such of these communications or abstracts of them as they may deem fit.

85. No report of any written or oral communication made to or proceedings of the Society at a Meeting shall be published except under the authority or by the permission of the Council.

Duties of Officers and Council.

A. *Of the President and Vice-Presidents.*

86. The President shall act as Chairman at all Meetings of the Society or of the Council at which he is present. In his absence one of the Vice-Presidents shall be chosen to discharge the functions of the President. If, at any Meeting of the Society or Council, neither the President nor one of the Vice-Presidents is present, some other Fellow of the Society shall be chosen Chairman for the occasion.

87. The President shall further discharge the several duties herein assigned to him.

B. *Of the Secretaries.*

88. It shall be the duty of the Secretaries to attend (one or both of them) at every Meeting of the Society and of the Council, to record the minutes of the proceedings, and to read these minutes at the next Meeting. They shall, under the direction of the President and Council, conduct the correspondence of the Society and issue all requisite notices to the Fellows for convening Meetings or otherwise, and perform such other duties as the President or Council shall assign to them.

C. *Of the Treasurer.*

89. The Treasurer shall keep a proper account of the income and expenditure of the Society in books to be provided for the purpose. He shall submit his accounts, with vouchers for payments made by him, to be audited once in each year, and shall produce the account-books, properly posted up, when required by the Council. He shall present to the Society at the Annual General Meeting a balance-sheet and report signed by the Auditors.

90. He shall keep an account of all such Fellows as shall have paid their annual subscriptions, and also of those who have paid a composition in lieu thereof. In this account shall be noted the times up to which the annual payments have been made, and the arrears of each Member.

91. Six weeks at the least before the day appointed for holding the Annual General Meeting the Council shall appoint two Fellows of the Society, not being Members of the Council, who shall audit the Treasurer's accounts and balance-sheet, and report thereon to the Society.

D. *Of the Council.*

92. The Council shall make provision for carrying out the objects of the Society, and for conducting its affairs in accordance with the Memorandum and Articles of Association. They shall, subject to the Regulations of the Society for the time being, have the sole control and management of the income, property, and affairs of the Society, and may appoint and dismiss any paid officers and servants.

93. Meetings of the Council shall be summoned by the Secretaries, under the direction of the President. Five Members shall form a quorum.

94. The Council shall meet at least once in each calendar month during a Session.

95. In addition to the Meetings mentioned in the last article, the President may at any time direct the Secretaries to summon a Special Meeting of the Council; and he shall direct a Special Meeting thereof to be summoned at any time upon a requisition addressed to him by three Members of the Council.

96. Questions arising before the Council shall be decided by a show of hands, except in any case in which a ballot shall be demanded, or in which a ballot is required by these Articles, and, in case of an equality of votes, the Chairman shall have a second or casting vote.

97. Any Member of the Council who shall be personally concerned in a question under consideration shall retire during the discussion and determination of the same.

98. If at any Meeting of the Council business be introduced of which notice has not been given either at the previous Meeting of the Council or in the summons calling the Meeting, any Member present shall be entitled to require that no vote or decision shall be taken on such business until the next Meeting of the Council; but, subject as aforesaid, any business may be transacted at a Meeting of the Council without notice of such business having been given.

99. The Council shall, at the Annual General Meeting, present to the Society a Report on the position of the Society, financially and otherwise, and on the affairs and proceedings of the Society generally during the previous year.

E. *Of the Investments of the Society.*

100. Such of the monies of the Society as shall not be required for the immediate purposes thereof may be invested from time to time by the Council (either in the name of the Society or in the name or names of such person or person son behalf of the Society as the Council may from time to time appoint) in any of the public Stocks or Funds or Government Securities of the United Kingdom or India, or in Bank of England Stock, or in or upon the Bonds, Mortgages, Debentures, Stocks, or Securities of any Municipal Corporation in Great Britain, or in or upon the Debentures, Preference Shares, or Stocks of any Railway Company in Great Britain or India, or upon any other Security that may be approved by the Society in General Meeting; with power to vary such investments for others of any kind hereby or hereafter to be authorized.

Notices.

101. A Notice may be served by the Society upon any Member, either personally or by sending it through the post in a prepaid letter addressed to such Member at his registered address.

102. Any Notice sent by post shall be deemed to have been served at the time when the letter containing the same would be delivered in the ordinary course of the post; and in proving such service it shall be sufficient to prove that the letter containing the Notice was properly addressed and put into the Post-Office.

103. Any Member residing out of the United Kingdom may name an address within the United Kingdom at which all Notices shall be served upon him, and all Notices served at such address shall be deemed to be well served. If he shall not have named such an address he shall not be entitled to any Notices.

Time and Place of Science Meetings.

At present Science Meetings of the Society are held at the Royal College of Science, Imperial Institute Road, South Kensington, on the second and fourth Fridays in the month during the months of November to June inclusive, with the exception, however, of the following Fridays—namely, the last two in December, the first two in January, Good Friday, and the first Friday after Good Friday. The Meetings held on the second Fridays are at 8 P.M., and those on the fourth Fridays at 5 P.M.

Office of the Society.

The Registered Office of the Physical Society of London is at No. 22 Albemarle Street, W.

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Vice-Presidents :

Secretaries :

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Demonstrator :

Ordinary Members of Council :

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Address of the President, C. CHREE, Sc.D., LL.D., F.R.S.